Characterising the physical state and textural stability of sugar gum pastes

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ABSTRACT

Water sorption and textural properties of four sugar gum pastes were investigated to characterise their physical state and textural stability when exposed to adverse %RH and/or temperature conditions. Dynamic vapour sorption (25 °C) and dynamic dewpoint isotherm (25 and 40 °C) methods showed that all gum pastes exhibit predominantly Type III sorption behaviour due to the presence of large amounts of crystalline sugars. Gum paste deliquescence points (RH_o) were influenced by sugar type, with the commercial materials (containing sucrose and glucose) exhibiting lower RH_o values than the lab-made materials (containing sucrose); and by storage temperature, with lower RH_o values at 40 °C compared to 25 °C. Changes in textural properties (hardness, distance to break, and structural integrity), signifying decreased gum paste stability, occurred concomitantly with the initial stages of increased water sorption, driven mainly by RH_o differences among the gum paste materials.

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1. Introduction

Sugar gum paste (referred to herein as gum paste) is a mixture of powdered confectioner's sugar (sucrose), gum, water, and—depending on the formulation—other substances, such as protein, other sugars, and shortening (Phillips, 2008). Current uses for gum paste range from cake decorations to faux flower arrangements to historical recreations (Mason, 2004). Although many gum paste creations are produced as temporary edible decorations, exposure to high relative humidity (%RH) and/or temperature conditions can appreciably affect their textural stability (Daniels & Lohneis, 1997).

Water sorption isotherms determine the amount of water sorbed by a material as a function of %RH at a constant, specified temperature and provide insight into the physical state of the solids (crystalline or amorphous) (Fennema, 1996). To date, no published literature characterising the water sorption behaviour of gum paste and the effect of that water on product stability was found in the databases searched. There are multiple factors that can affect the water sorption behaviour of gum paste. These include the physical state of the gum paste ingredients, especially sugar(s); the type(s) of sugar(s) present; the contribution to sorption by other ingredients, such as gum and protein; and ingredient interactions, such as between sugar and protein.

Powdered confectioner's sugar[2] (sucrose) is the major ingredient in gum paste, thus the physical state of the sucrose (crystalline, amorphous or a combination) plays a key role in determining the gum paste water sorption behaviour. Standard crystalline sucrose (mean sieve aperture 630 µm) has been shown to exhibit a type III,[3] or J-shaped, isotherm; whereas amorphous sucrose has been shown to exhibit a type II, or sigmoidal-shaped, isotherm, until enough water is adsorbed to promote crystallisation of the amorphous sucrose. This moisture-induced crystallisation from the amorphous state subsequently results in a type III sorption isotherm (Bell & Labuza, 2000; Yu, Kappes, Bello-Perez, & Schmidt, 2008). Moreyra and Peleg (1981) obtained an isotherm of powdered sucrose (crystal size 75–150 µm; no added corn starch) using saturated salt slurries in desiccators (temperature not specified). They observed a gradual increase in water sorption from 0.22 to 0.62 a_w, followed by a marked increase in water sorption after ~0.75 a_w, as the powdered sucrose dissolved. They postulated that the relatively high hygroscopicity of the powdered sucrose at low a_w values, compared to standard sucrose, might be caused by the presence of impurities. However, production of powdered sugar involves extensive grinding in hammer mills (Asadi, 2007; Dunshee 1974), which has been documented to lead to the formation of amorphous regions on the surface of

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[2] Specifications for 10X powdered sugar indicate that 97 to 98% of the sugar must pass through a US 200 screen (Asadi, 2007), which has a sieve aperture of 74 µm (Perry, Chilton, and Kirkpatrick (1963)). Due to the fine particle size and caking tendency of powdered sugar, an anti-caking agent, such as corn starch, is added, typically at 3% w/w (Asadi, 2007).
[3] According to the isotherm classification scheme developed by Brunauer, Deming, Deming, and Teller (1940).

crystalline sucrose (Rogé & Mathlouthi 2000, 2003), a problem also encountered in the manufacture of pharmaceutical excipients (Ahlneck & Zografi, 1990; Lappalainen, Piktänen, & Harjunen, 2006). Thus, we postulate that the presence of small regions of amorphous material formed during the grinding process was responsible for a sorption behaviour observed by Moreyra and Peleg (1981) at the low a_w values. However, the influence of this small amount of amorphous material in powdered sugar on the water sorption properties of the gum paste is not yet known.

In addition to the physical state of the sucrose, the presence and type of other sugars also affects isotherm behaviour. Crystalline solids, such as crystalline sucrose, exhibit deliquescence, which is a first-order phase transition from solid to solution, induced by water uptake from the atmosphere (Salameh, Mauer, & Taylor, 2006; Salameh & Taylor, 2006; Zografi & Hancock 1994). The point at which deliquescence begins is termed the critical relative humidity (RH_o). RH_o is unique to each crystalline solid and is a function of temperature, where, in general, the higher the temperature the lower RH_o (Seinfeld & Pandis 1998; Van Campen, Amidon, & Zografi, 1983). A recent study by Salameh et al. (2006) demonstrated that mixing two or more chemically different deliquescent food ingredients results in a lowering of RH_o. For example, a 50:50 mixture of crystalline sucrose, which has a RH_o of 85% at 25 °C, and α-glucose monohydrate, which has a RH_o of 91% at 25 °C, exhibited a RH_o of 79% at 25 °C. In addition to powdered sugar (sucrose), some gum paste formulations include other sugars, such as glucose,[4] corn syrup, or corn syrup solids, which according to the deliquescent lowering data reported by Salameh et al. (2006), would result in a decreased deliquescence point compared to using powdered sugar (sucrose) alone.

The presence of additional ingredients, such as gum(s) (e.g., tragacanth and gum arabic) and proteins (e.g., egg white or gelatin), and their interaction with the sugars present, as well as each other, may also contribute to the water sorption behaviour of the gum paste. Generally, gums and proteins exhibit type II (sigmoidal) water sorption isotherm behaviour (Bifani & Briceno, 2002; Cadden, 1988, Labuza & Altunakar, 2007; Wallingford & Labuza, 1983). However, it is not yet known whether the change in water sorption, due to additional ingredients, will significantly affect the deliquescence point of the sugar(s) and/or the textural properties of the finished gum paste.

In addition to its importance in isotherm behaviour, a_w plays a major role in determining the texture of food material. For example, Katz and Labuza (1981) observed that both crispness intensity and consumer liking of snack food products (measured by both mechanical and sensory methods) decreased when the a_w of the snack food approached and passed a characteristic critical a_w. Although a few techniques exist for minimising the effect of increasing %RH on gum paste stability [for example, increasing the amount of gum in a formulation or spraying with a food grade lacquer (Wilton, 2009)], no systematic characterisation of the effects of %RH and temperature on the texture and structural integrity of gum paste was found in the literature.

Thus, the major objective of this study was to investigate the textural stability issues associated with gum pastes by: (1) characterising their physical state (crystalline or amorphous or both) by analysing their water sorption behaviour using recently developed automated water sorption technologies (Dynamic Vapour Sorption and Dynamic Dewpoint Isotherms) and (2) determining their textural properties under adverse %RH and temperature conditions using instrumental methods.

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[4] The deliquescence point of glucose varies with form, where α-glucose anhydrous and α-glucose monohydrate have the same RH_o of 91% at 25 °C, whereas β-glucose has a RH_o of 74% at 25 °C (Salameh et al., 2006).

2. Materials and methods

2.1. Materials

$10\times$ powdered sugar (Domino, Yonkers, NY), spray-dried gum arabic (Coyote Brand, Gum Technologies, Tuscon, AZ), and filtered water (Absopure, Urbana, IL) were used "as is". Dry nitrogen gas (SJ Smith, Urbana, IL) was used for both DVS and DSC experiments. All gum paste formulations were made according to commonly accepted procedures or manufacturer's directions with one exception: addition of shortening to the work surface to improve paste (also termed dough) workability. However, shortening was not added due to inherent difficulties in quantifying the amount of shortening that each material would pick up and due to the potential interference of the shortening on the water sorption isotherm behaviour.

2.1.1. Lab-made gum paste

Two hundred grams of $10\times$ confectioner's sugar was mixed with 7.5 g gum arabic and 26 ml of spring water in a glass dish using a metal spoon to make a pliable dough. Fifty grams of $10\times$ confectioner's sugar was then kneaded into the dough by hand until incorporated; then wrapped in plastic wrap and stored in an airtight container at 4 °C until use. Table 1 shows the % composition of the ingredients.

2.1.2. Lab-made gum paste with protein

Sixty-six grams of egg whites (moisture content 88% wet basis), separated from two eggs, were mixed on high using a stand mixer with a flat paddle attachment for 10 s to break up the egg whites (Lodge 2001). After breaking up the egg whites, the mixer speed was reduced to the lowest speed setting and 500 g of $10\times$ confectioner's sugar was slowly added and mixed until a thick dough formed. Fifteen grams of gum arabic was sprinkled over the dough and mixed on low speed until incorporated. The gum paste was kneaded by hand for 1 min and then wrapped in plastic wrap and stored in an air-tight container at 4 °C until use. Table 1 shows the % composition of the ingredients.

Table 1
Percent composition of lab-made and lab-made with protein gum pastes and ingredient lists for commercial Ready-To-Use gum paste and commercial Powdered gum paste mix.

	Lab-made	Lab-made with protein
% Composition of lab-made gum pastes		
$10\times$ powdered sugar	88%	86%
Gum arabic	3%	3%
Egg white	–	1%
Water	9%	10%
Ingredient list for Commercial Ready-To-Use gum paste		
Sugar		
Corn syrup		
Water		
Carboxy methyl cellulose		
Gum tragacanth		
Gum arabic		
Tartaric acid		
Artificial vanilla flavor		
Potassium sorbate		
Titanium dioxide		
Ingredient list for Commercial Powdered gum paste mix[a]		
Confectioner's sugar		
Dextrose (glucose)		
Corn syrup solids		
Sodium alginate		

[a] The consumer is instructed to add 1/4 cup water to 1 lb of Powdered mix and 1/3 cup additional powdered sugar.

2.1.3. Commercial gum pastes

Wilton (Woodridge, IL) Ready-To-Use (RTU) sugar gum paste and Wilton Powdered Gum Paste Mix were used as example commercial products. RTU gum paste was used "as is". Powdered gum paste was made following the manufacturer's instructions. In short, 200 g of gum paste powder was mixed with 26.5 ml of water in a glass dish using a metal spoon to make a pliable dough. The dough was then tightly wrapped with plastic wrap and allowed to rest under room conditions for 15 min. After resting, 23 g 10× confectioner's sugar was kneaded into the dough by hand until incorporated; then wrapped in plastic wrap and stored in an airtight container at 4 °C until use. Table 1 shows the ingredient list for both RTU and Powdered gum pastes.

2.2. Methods

2.2.1. Gum paste disc preparation

Gum paste discs were made by allowing the gum paste to warm to room temperature and then rolling through a pasta machine (Norpro, Everett, WA). Gum paste was rolled at thickness settings 1–5 to achieve a final thickness of approximately 2 mm. RTU gum was rolled at setting 5 twice, since it was more elastic than the other gum paste materials and required two rollings at setting 5 to achieve the desired end thickness. Between rollings, the gum paste was covered with plastic wrap to prevent it from drying out, while the rollers were gently cleaned with distilled water and dried. Discs for DVS analysis and for DSC analysis were made using a 0.6 cm diameter cylinder. The 0.6 cm diameter discs were allowed to dry under room conditions for 2 h (until rigid enough to handle) and then placed over $MgCl_2$ (33% RH) in proximity equilibration cells (PEC) at 25 °C for 2 days to obtain a uniform starting %RH before DVS isotherm determination. 33% RH was selected as the uniform starting %RH, since it is a good approximation of the average yearly indoor %RH. Discs for Dynamic Dewpoint Isotherms (DDI) were made using a 3.2 cm diameter cap. The 3.2 cm diameter discs were allowed to dry under room conditions for 2 h (until rigid enough to handle) and then placed over $MgCl_2$ (33% RH) in PEC at 25 °C for 4 days to obtain a uniform starting %RH before DDI determination. Discs for texture analysis were made using a 5.1 cm diameter round cookie cutter. The 5.1 cm diameter discs were allowed to dry under room conditions for 4 h (until rigid enough to handle) and then placed over $MgCl_2$ (33% RH) in a desiccator at 25 °C for 7 days to obtain a uniform starting %RH.

2.3. DVS analysis

2.3.1. DVS pan preparation and instrument calibration

Prior to use, the DVS pans were cleaned with water and ethanol and the following static elimination protocol was carried out. Pans were placed in the DVS instrument and exposed to 95% relative humidity (RH) for 20 min to remove static electricity, followed by 0% RH for an additional 20 min to dry the pans (Garcia 2005). Pans were then exposed to 33% RH until the weight stabilised and the balance was teared before sample addition. The balance was calibrated at 25 °C with standardised weights and the mass flow controllers were calibrated by Surface Measurement Systems (London, UK) and verified at 25 °C according to the manufacturer's directions using three salts, LiCl (11.3%), $MgCl_2$ (32.8%) and NaCl (75.3%).

2.3.2. DVS moisture contents

Moisture contents of the four gum paste materials and the 10× powdered sugar was determined in duplicate using a Dynamic Vapour Sorption (DVS) 1000 (Surface Measurement Systems, London, UK). For gum paste materials, a 0.6 cm disc, weighing approximately 36 to 46 mg, was placed in a mesh pan and placed into the DVS instrument at 33% RH, corresponding to the initial %RH. For 10× powdered sugar, approximately 5 mg of sugar was placed in a glass round-bottom pan and placed into the DVS instrument also at 33% RH. A 2-step special automatic operation method was created for each material type: a dm/dt of 0.00005%, with a minimum stage time of 5 min and a maximum stage time of 2000 min was used for the 33% RH value to maintain the uniform starting %RH; and a stage time of 2800 min (lab-made and 10× powdered sugar materials) or the maximum stage time of 9999 min (commercial materials) was used for the 0% stage to obtain the dry weight, since water from the commercial materials took longer to remove than the lab made materials. The airflow in the DVS was set at 500 standard cubic centimeters per minute (sccm) for lab-made materials and at 750 sccm for commercial materials. Moisture content determinations were done in duplicate (Table 2).

2.3.3. DVS working water sorption isotherms

DVS working isotherms were obtained in duplicate for the four gum paste materials and for the 10× powdered sugar using a DVS 2000 (Surface Measurement Systems, London, UK). For each gum paste isotherm determination, a 0.6 cm diameter sample disc (prepared as described under the Gum paste disc preparation section) was placed on a quartz flat-bottom pan and equilibrated to 33% RH in the DVS to maintain the uniform starting %RH, followed by exposure to seven target humidity values: 43%, 58%, 69%, 75%, 80%, 82% and 84% to obtain the upper portion of the working isotherm or to two target humidity values: 23% and 11% to obtain the lower portion of the working isotherm. The 10× powdered sugar was placed over $MgCl_2$ (33% RH) in PEC at 25 °C for at least 2 days to obtain a uniform starting %RH before isotherm analysis. For each 10× powdered sugar isotherm determination, approximately 15 mg of powdered sugar was placed in a round-bottom pan, instead of a flat-bottomed plan, which prevents the sample from blowing off the pan, and equilibrated to 33% RH in the DVS before being exposed to the target RH values. A dm/dt of 0.00005% with a minimum stage time of 5 min and maximum stage time of 2000 min was used for all target relative humidity levels. The airflow in the DVS was set at 500 sccm for all isotherm experiments.

After each experiment, the data were exported to Microsoft Excel for analysis using a DVS macro. The change in mass for the last ten stabilised weight change readings for each duplicate at each %RH level were converted to % moisture content (% MC) dry basis ([g water/g dry solid] * 100). The duplicate % moisture content (db) at each %RH level were then averaged and plotted as a function of its DVS target %RH. The deliquescence point was determined by calculating the intersection point between the linear sorption portion of the isotherm before and the linear sorption portion of the isotherm after the onset of deliquescence according to the method of Salameh and Taylor (2005).

2.4. DDI working water sorption isotherms

Dynamic dewpoint working isotherms (DDI) were obtained in duplicate for gum paste and 10× powdered sugar materials using an AquaSorp Isotherm Generator (Decagon Devices, Pulllman,

Table 2
Percent moisture content (dry basis) and associated standard deviations (SD) of gum pastes and 10× powdered sugar equilibrated to 33% RH and 25 °C.

Materials	% MC (db)	SD
Lab-made	0.783	0.1414
Lab-made with protein	0.867	0.0315
RTU	1.325	0.0311
Powdered	0.130	0.0823
10× Powdered sugar	0.300	0.0598

WA, firmware version ASIG 1.12). Isotherms for each gum paste material (3.2 cm diameter sample discs prepared as described under the Gum paste disc preparation section) and for $10\times$ powdered sugar (800 mg which was placed over $MgCl_2$ [33% RH] in PEC at 25 °C for at least 2 days to obtain a uniform starting a_w before isotherm analysis) were obtained between 0.03 and 0.33 a_w (lower isotherm portion) and 0.33 to 0.84 a_w (upper isotherm portion) at 25 °C and between 0.03 and 0.33 a_w and 0.33 to 0.83 a_w (with the exception of Powdered gum paste, which was stopped at 0.81 a_w, since at that a_w it was well passed its deliquescence point) at 40 °C. The flow rate was set to 50 ml/min. The isotherm moisture contents were calculated using the DVS determined-moisture content (dry basis). Since each DDI run is unique, duplicate runs were plotted. The deliquescence point was determined as mentioned previously.

2.5. Amorphous solids detection

Differential scanning calorimetry (DSC) and hyper differential scanning calorimetry (hDSC) measurements were done using a DSC Q2000 (TA Instruments, Newcastle, DE) using Tzero hermetically sealed aluminum pans and lids to detect the presence of amorphous solids in "as is" $10\times$ powdered sugar. Sample weights were 5 ± 1 mg. For DSC, samples were cooled from 25 °C to −65 °C, held at -65 °C for 5 min and then heated from −65 °C to 210 °C at a heating rate of 10 °C min^{-1}. Duplicate DSC scans were done. For hDSC, samples were heated from 25 °C to 60 °C at a heating rate of 10 °C min^{-1} and then held at an annealing temperature of 60 °C for 300 min. After annealing, samples were cooled to −10 °C, and then heated from −10 °C to 210 °C at a rate of 100 °C min^{-1} according to the method reported by Lappalainen, Piktänen, and Harjunen (2006). Due to poor reproducibility, nine hDSC scans were done.

2.6. Texture analysis

Texture analysis was performed using a TA-XT2 (Texture Technologies, Scarsdale NY), on 5.1 cm diameter gum paste discs (prepared as described under the Gum paste disc preparation section), using a three-point bend mechanical test to determine hardness and distance to break. After being stored over $MgCl_2$ (33% RH) at 25 °C for 7 days in desiccators to obtain a uniform starting %RH, samples were transferred to PEC containing saturated salt slurries at various %RH values (Table 3) and stored at either 25 °C or 40 °C overnight (22 h) in a constant temperature chamber.

Samples were removed from the PEC immediately before running the test protocol to minimise effects of ambient conditions on sample %RH. Test option "Rupture Test" was used with a pre-test speed of 2.0 mm/s and a test speed of 0.2 mm/s. Data were collected at 400 points per second. Hardness was measured by maximum force and distance to break was measured at maximum force, where increasing distance indicates decreasing brittleness.

Statistical analysis, using proc GLM and least squares means analysis in SAS 9.1 (Cary, NC), on hardness and distance to break was done using the model:

$$Y_{ijk} = \mu + \tau_i + \tau_j + \tau_{ij} + \varepsilon_{ij} \qquad (1)$$

where i is the material type and j is the %RH. τ_i and τ_j represent the main effects, τ_{ij} represents the interaction and ε_{ij} represents the error. Multiple comparisons were done and p-values were adjusted using the Holm (step-down Bonferroni) method to determine the significance of interactions for both hardness and distance to break within material type and between %RH values. A p-value of 0.05 was used.

2.7. Loss of structural integrity

Measurement of the effect of increasing %RH values on structural integrity of gum paste on 5.1 cm diameter discs (prepared as described under the Gum paste disc preparation section) was performed using modified aluminum pans in PEC containers. A 4 cm diameter opening was cut in the aluminum pans so the gum paste discs could rest on the pan edges, but were completely unsupported in the middle to allow detection and measurement of loss of structural integrity ("sag"). After being stored over $MgCl_2$ (33% RH) at 25 °C for 7 days in desiccators to obtain a uniform starting %RH, samples were transferred to PEC containing saturated salt slurries at various %RH values (Table 3) at 25 °C or 40 °C overnight (22 h) in a constant temperature chamber. After 22 h, distance of "sag" from the pan edge was measured using calipers and samples were photographed. Samples were returned to their experimental %RH and temperature conditions and measured again at 48, 72 and 96 h. Six replicates were done for each gum paste material. The standard deviation (SD) for the sag test data ranged from $\pm$ 0.30 to 3.2 mm.

3. Results and discussion

3.1. Water sorption isotherm behaviour

DVS working water sorption isotherms for the four gum paste and $10\times$ powdered sugar (sucrose) materials are shown in Fig. 1. All of the gum paste materials exhibited type III (J-shaped) isotherm behaviour, similar to that of the $10\times$ powdered sugar base material, indicating that water sorption was dominated by the crystalline materials present in the gum pastes. Each gum paste tested exhibited minimal water sorption below 60% RH, similar to the powdered sugar base material, and maintained the same order of % MC at each %RH value; that is, RTU had the highest % MC, lab-made with protein had the second highest % MC, followed by lab-made with the third highest and Powdered had the lowest % MC. Above 60% RH, however, the water sorption isotherm behaviour of the gum pastes depart from each other and from that of the $10\times$ powdered sugar base material. From 69% RH through the final %RH point of 84%, all materials, except the Powdered material, exhibited the same% MC order as below 60% RH. The Powdered material transitioned from lowest to highest % MC between 60% RH and 75% RH, and maintained the highest % MC through 84% RH.

The dramatic increase in % MC observed in the gum pastes above 60% RH is mainly attributed to water sorption by the crystalline sugar(s) present as they pass through their deliquescence point (RH_o); but, is also influenced by the sorption of water by other hygroscopic materials present. The deliquescence points determined from the DVS gum paste and $10\times$ powdered sugar isotherms at 25 °C are given in Table 4. For the lab-made materials (with and without protein), the deliquescence points are only slightly lower than the deliquescence point of the $10\times$ powdered sugar, indicating that the sorption behaviour of the lab-made materials is driven by the deliquescence behaviour of the $10\times$ powdered sugar base material contained in these gum paste mate-

Table 3
%RH values at 25 °C and 40 °C for select saturated salt slurries (values rounded from those reported by Greenspan (1976)).

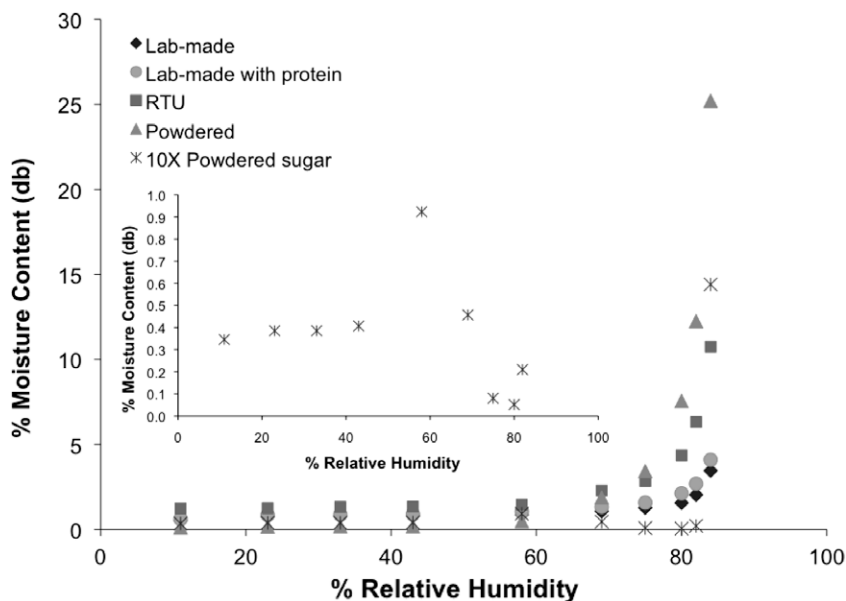| Saturated Salt	%RH at 25 °C	%RH at 40 °C
$MgCl_2$	33	32
NaBr	58	53
KI	69	66
NaCl	75	75
KBr	81	79
KCl	84	82

Fig. 1. DVS working water sorption isotherms of lab-made, lab-made with protein, Ready-To-Use, Powdered gum paste and 10× powdered sugar materials at 25 °C. The insert shows 10× powdered sugar sorption behaviour between 11% and 82% RH at 25 °C.

rials. However, for the RTU and Powdered materials, the deliquescence points are much lower than the deliquescence point of the 10× powdered sugar, due to the presence of more than one sugar type in these gum paste materials (Table 1), as well as deliquescence point lowering as documented by Salameh et al. (2006). Glucose, in the form of dextrose, corn syrup or corn syrup solids, is most likely included in the commercial materials to extend the workability of the gum paste (dough) as was observed during sample preparation. However, as demonstrated by the decrease in the deliquescence points for the commercial materials, addition of glucose decreases the stability of the finished gum paste product when exposed to high %RH and temperature conditions.

Although water sorption above 60% RH was predominantly driven by the deliquescence event associated with the crystalline sugar(s) present in gum paste materials, the presence of other hygroscopic materials also influenced the water sorption behaviour. For example, the presence of egg white protein in the lab-made gum paste resulted in a slightly higher % MC than in the lab-made gum paste without egg white protein. What is not yet known is whether the presence of other ingredients, such as gum or protein, effects only the amount of water sorbed by the gum paste material or if it also results in deliquescence lowering, as discussed above for crystalline materials.

In addition to DVS isotherms, isotherms were also obtained using the Dynamic Dewpoint Isotherm (DDI) method, which allowed for the rapid acquisition of isotherms at the two temperatures of interest (25 °C and 40 °C) with a sizable number of data points (>70) (Carter & Fontana, 2008). Working DDIs for the four gum pastes and 10× powdered sugar are shown in Fig. 2 and associated DDI deliquescence points are given in Table 4. In general, the DDIs followed the same trends as observed for the DVS isotherms.

DDI deliquescence points at 25 °C also followed the same trends as those obtained for the DVS isotherm at 25 °C, with the lab-made materials yielding higher deliquescence points than the commercial materials. The DVS obtained deliquescence points were slightly lower than the DDI obtained values for the commercial materials (a difference of 1.6% and 3.0% RH for RTU and Powdered, respectively) and the 10× powdered sugar (a difference of 1.3%), which is attributed to two factors: (1) the smaller number of DVS isotherms points obtained, which limited our selection of data point ranges used in the deliquescence point calculation, and (2) the difference between the two isotherm methods. Samples analysed by the DVS are allowed to come to steady state equilibrium (*via* the dm/dt criterion) at each selected %RH value before exposure to higher (adsorption) or lower (desorption) %RH values. Waiting for steady state equilibrium at each %RH results in longer run times, however it allows time for both primary (surface) and secondary (bulk) water vapour diffusion in (adsorption) or out of (desorption) the gum paste sample. In contrast, the DDI method begins measuring sample a_w directly after the sample is exposed to a user determined amount (*via* the flow rate) of water-saturated air (a_w measurement time of approximately 5 min for most materials), reflecting near real-time changes in the a_w of the sample surface, but, depending on the nature of the material, does not always allow time for slow bulk diffusion. For the gum paste materials studied here,[5] the DDI exhibited lower % MCs in the elbow region of the isotherm compared to the DVS obtained isotherms; however, the DDIs rejoined the DVS isotherms above the deliquescence event. In the case of the lab-made and lab-made with protein gum paste materials, only slight % MC differences were observed in the elbow region; whereas more considerable differences were observed for the commercial materials, with the Powdered material exhibiting

Table 4
Deliquescence points (RH$_o$) and associated standard deviations (SD) obtained at 25 °C from DVS and DDI isotherms and at 40 °C from DDI isotherms for the four gum paste materials and 10× Powdered sugar.

Materials	DVS 25 °C		DDI 25 °C		DDI 40 °C	
	RH$_o$	SD	RH$_o$	SD	RH$_o$	SD
Lab-made	81.1	0.40	80.6	0.020	72.6	0.17
Lab-made with protein	80.6	0.09	80.6	0.043	73.1	1.23
RTU	70.6	0.33	72.2	0.015	69.3	0.29
Powdered	67.8	0.31	70.8	0.006	67.4	0.86
10× Powdered sugar	82.0	0.04	83.3	0.069	81.1	0.02

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[5] This verbal comparison of the DVS and DD isotherms at 25 °C is augmented by viewing the individual gum paste graphs located in the Water sorption isotherm behaviour and hardness section (Fig. 5).
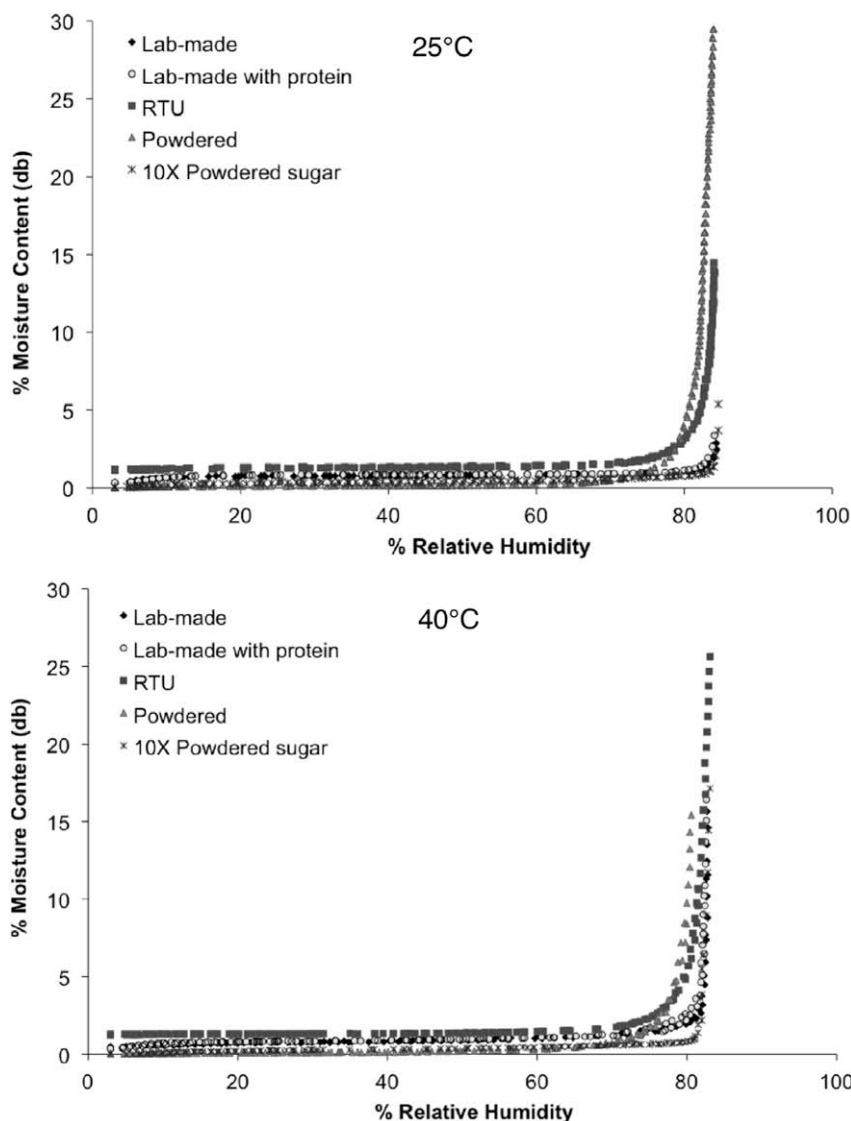
Fig. 2. Dynamic Dewpoint working isotherms of lab-made, lab-made with protein, RTU, Powdered gum pastes and 10× powdered sugar materials at 25 °C and 40 °C. Note: Duplicates are graphed, since each DDI run is unique.

the largest difference. Lee and Schmidt (2008) reported a divergence in water sorption isotherm behaviour between saturated salt slurry (a steady state method) and DDI methods at 25 °C for corn flakes (between 0.4 and 0.7a_w), but not for microcrystalline cellulose. They attributed the divergence to the slow diffusion of water into the corn flakes in the glassy to rubbery transition region. The divergence between the two isotherm methods provides a kinetic profile of water sorption responses from near real-time (DDI) to steady state (DVS) to increases in %RH.

As predicted by theory (Seinfeld & Pandis, 1998), the DDI obtained deliquescence points were lower at 40 °C compared to 25 °C. Thus, the higher the temperature the lower the %RH at which the gum pastes will begin to dramatically sorb water. It is interesting to note that the deliquescence points for the lab-made materials exhibited a much larger decrease (8.0% and 7.5% RH) compared to the commercial materials (2.9% and 3.4% RH) and the 10× powdered sugar (2.2% RH) between the two temperatures. Further investigation is needed in order to explain the underlying mechanism behind this large decrease in the deliquescence points for the lab-made materials, since it appears that the 10× powdered sugar is not responsible for the decrease. One possibility is that water

sorption by gum arabic is facilitated at the higher temperature in the lab-made materials, decreasing the apparent beginning of the deliquescence point.

3.2. Amorphous solids detection

Analysis of 10× powdered sugar by DSC showed no step change in heat capacity (i.e., no glass transition), indicating that the material was completely crystalline. In contrast, DVS analysis indicated that some amorphous sucrose was present in the 10× powdered sugar, as exhibited by an initial increase in moisture content up to 58% RH, followed by subsequent water loss at 69–80% RH (Fig. 1 insert). Traditional DSC may lack sufficient sensitivity in detecting small quantities of amorphous content (less than ∼10%). However, detection of small quantities of amorphous materials in predominantly crystalline materials has recently been reported by Saunders, Podluii, Shergill, Buckton, and Royall (2004) and Lappalainen et al. (2006) using hDSC. The fast scanning rates used in hDSC increase instrument sensitivity, thereby increasing the ability to observe small transitions. In this study, only one of the nine hDSC 10× powdered sugar scans exhibited a step change

in heat capacity between 91.6 °C and 94.6 °C, with the midpoint at 93 °C. The lack of reproducibility in the hDSC scans may be due to the small sample sizes used in hDSC, as well as the large amount of variation encountered in product handling and ambient conditions during the manufacturing and transport of powdered sugar.

Unlike the 10× powdered sugar, the DVS and DDIs for the gum pastes materials did not exhibit water gain and subsequent loss indicating that the finished gum paste contained no amorphous sucrose. This lack of detection of amorphous sucrose in the finished gum paste is most likely due to moisture-induced recrystallisation of the amorphous sucrose and/or crystallisation of any dissolved amorphous sucrose via the water added during gum paste making and the subsequent slow room temperature drying conditions employed in gum paste making.

3.3. Effect of %RH and temperature on textural properties

Texture analysis was done to investigate the practical effects of exposure to various %RH and temperature combinations, such as those experienced in tropical climates or under summer conditions, on the stability of gum paste discs. Texture analysis results are plotted as a function of %RH at 25 °C and 40 °C (Fig. 3). Texture analysis was not carried out at 11% and 23% RH, since water desorbs from the materials to achieve these %RH values; thus, no adverse textural effects were expected at these %RH values.

Only the lab-made gum paste showed no statistical differences in hardness as %RH increased, at both 25 °C and 40 °C. In contrast, hardness of lab-made with protein, RTU and Powdered materials significantly decreased at or above 69% RH (25 °C)/66% RH (40 °C)

(Fig. 3A and C). It is interesting to note that at both 25 °C and 40 °C RTU gum paste exhibited a significant increase in hardness as measured by force to break the gum paste discs from 33% RH/ 32% RH to 69% RH/66% RH, followed by a significant decrease in hardness at higher %RH values (Fig. 3A and C). Lab-made and lab-made with protein gum paste materials exhibit a similar, but not statistically significant, trend at 25 °C. Martínez-Navarrete, Moraga, Talens, and Chiralt (2004) observed similar behaviour in wafers, with the force required to break increasing from 0.113 a_w to 0.430 a_w (20 °C), and decreasing thereafter. The authors attributed the increase in force to an increase in sample deformability, which allowed the sample to increase its resistance to fracture. Heidenreich, Jaros, Rohm, and Ziems (2004) also observed an increase in the force required to break extruded rice crisps as a_w increased from 0.051 to 0.575 (25 °C). Pittia and Sacchetti (2008) have recently reviewed this antiplastisation effect of water in amorphous foods.

At 25 °C and 40 °C, lab-made and lab-made with protein gum paste materials exhibited no differences in distance to break as %RH increased (Fig. 3B and D). In contrast, distance to break of RTU and Powdered materials at both 25 °C and 40 °C significantly increased as %RH increased above 69% RH (25 °C)/66% RH (40 °C) (Fig. 3B and D).

3.4. Effect of %RH and temperature on structural integrity

Texture analysis showed that increasing %RH affected the hardness and distance to break of gum paste materials; during analysis, a loss of structural integrity was observed in some samples. Thus,
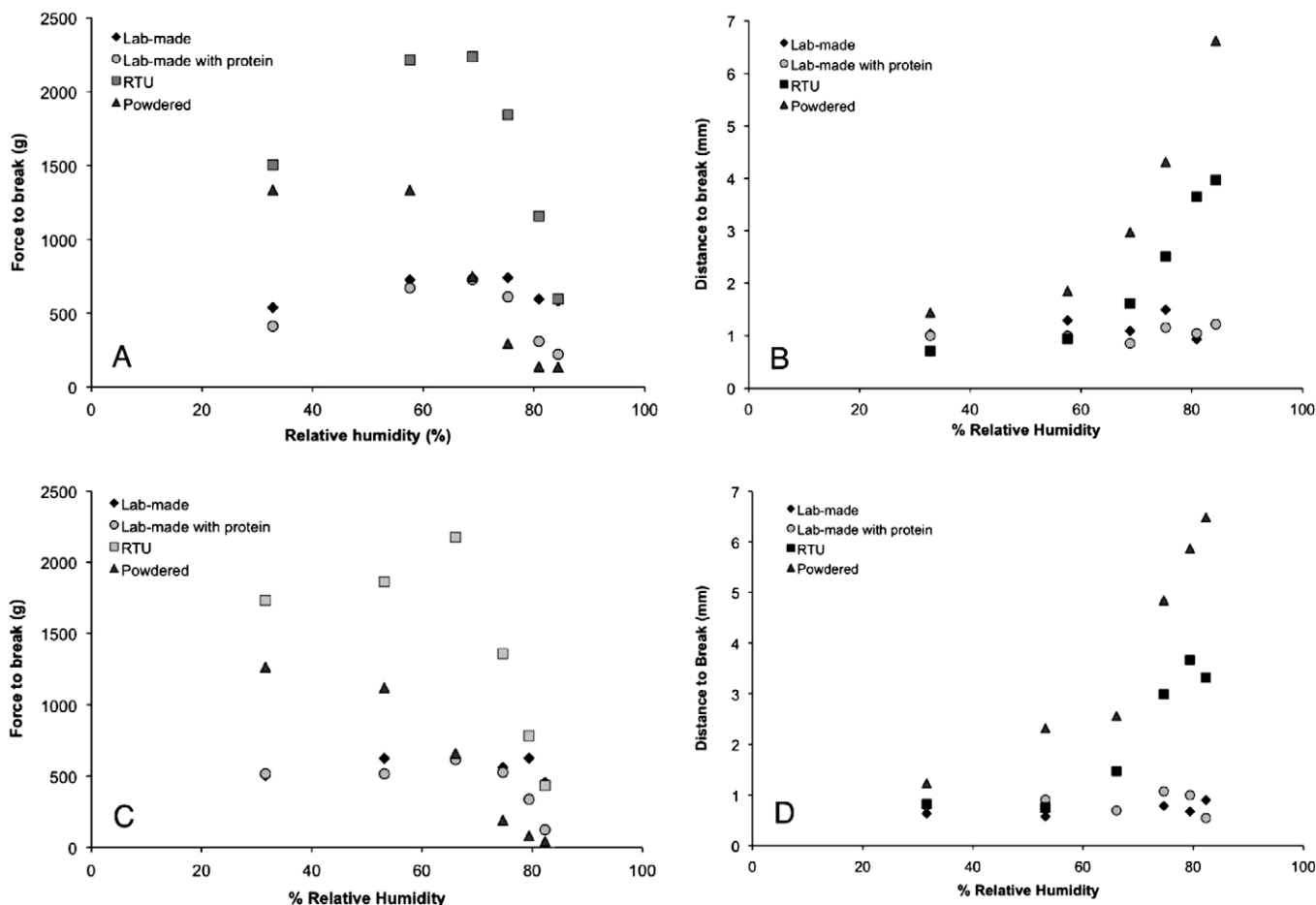

Fig. 3. Effect of increasing %RH on gum paste disc texture stored at 25 °C and 40 °C for 22 h: (A) hardness, 25 °C, (B) distance to break, 25 °C, (C) hardness, 40 °C, and (D) distance to break, 40 °C.

Table 5
Effect of storage %RH and temperature on structural integrity measured as "sag" in mm from initial position for the four gum paste materials.

Storage time	"Sag" in mm after storage at specified % RH and temperature							
% RH (25 °C/40 °C)	Lab-made		Lab-made with protein		Commercial ready-to-use		Commercial powdered	
	25 °C	40 °C	25 °C	40 °C	25 °C	40 °C	25 °C	40 °C
22 h								
75/75	0	0	0	0	0	0	0	1.5
80/79	0	0	0	0	0	0	0.5	3.3
84/82	0	0.4	0	0	0	0.5	2.7	4.3[a]
48 h								
75/75	0	0	0	0	0	0	0	3.3
80/79	0	0	0	0	0	0	2.8	4.0[a]
84/82	0	1.4	0	0.3	0	1.3[a]	5.0[a]	5.3[a]
72 h								
75/75	0	0	0	0	0	0	0.6	3.2
80/79	0	0	0	0	0	0	3.8	4.8[a]
84/82	0	1.4[b]	2.0	1.2[b]	0	2.5[a]	6.1[a]	7.0[a]
96 h								
75/75	0	0	0	0	0	0	1.5	3.8
80/79	0	0	0	0	0	0	4.5	5.2[a]
84/82	0	1.3	2.6	1.5	1.8	3.3[a]	7.3[a]	9.3[a]

[a] Samples were sticky to the touch on the side closest to the saturated salt solution.
[b] One of six replicates exhibited complete collapse.

the effect of increasing %RH and temperature on structural integrity of gum paste materials was determined by measuring millimeters of sample "sag" from the initial position, the sample pan edge (Table 5). At 25 °C, lab-made samples showed no sag at any %RH value over the 96-h testing period. Lab-made with protein samples showed no sag, except at the 84% RH value at 72 and 96 h of storage. When the temperature was increased to 40 °C, all samples, except lab-made with protein, showed sag at 22 h of storage at 82% RH. After 72 h of storage at 82% RH, one lab-made and one lab-made with protein replicate completely collapsed, with the sample falling through the opening in the aluminum pan into the saturated salt slurry. However, the other replicates continued to exhibit a small amount of sag through 96 h of storage.

At 25 °C, RTU showed no sag until 96 h of storage at 84% RH, whereas at 40 °C, RTU showed sag after only 22 h of storage at 82% RH. In contrast, the Powdered material showed sag very early

Fig. 4. Effect of 84% RH, 40 °C storage on structural integrity measured as "sag" in mm from the initial position of the Powdered gum paste for one replicate (Table 5).

in the testing period (Fig. 4). Specifically, at 25 °C, the Powdered samples showed sag at and above 80% RH after 22 h of storage, and even showed sag at 75% RH after 72 h of storage. At 40 °C, all Powdered samples showed sag at and above 75% RH after only 22 h of storage (Table 5). Surprisingly, none of the RTU or Powdered samples exhibited complete collapse during the testing period – this difference between the behaviour of the lab-prepared materials and commercial materials is mostly likely due to the amount and type of gum(s) used in the formulation.

It is interesting to note that in addition to sag, RTU materials stored at 82% RH (40 °C) and Powdered materials stored at 84% (25 °C) and at 75% and 82% RH (40 °C) became sticky to the touch after storage (Table 5). The development of stickiness was time dependent, for example, RTU stored at 82% RH (40 °C) did not exhibit stickiness until after 48 h of storage. Stickiness is probably caused by the material passing the RH_o and beginning to go through deliquescence. As gum paste materials are exposed to RH levels at and above RH_o, crystalline sugar on the material surface begins to dissolve and go into solution.

3.5. Water sorption isotherm behaviour and hardness

To further examine the relationship between water sorption isotherm behaviour and textural properties, DVS and DDI isotherms and hardness, all at 25 °C, were plotted as a function of %RH for each gum paste material (Fig. 5). For the lab-made with protein, RTU, and Powdered materials, the statistically significant decrease in hardness (discussed previously) occurred concomitantly with the initial stages of increased water sorption associated with the deliquescence of the crystalline sugar(s) present, as well as water sorption by other hygroscopic materials present in the formulas, for both DVS and DDI methods. As mentioned previously, hardness for the lab-made gum paste was not statistically different as a function of %RH; however, it appears (Fig. 5A) that hardness was beginning to decreases at the high %RH values and would most likely become statistically significant if the storage %RH value was increased slightly, to just above 84% RH.

Even though both DVS and DDI methods exhibit an increase in % MC concomitantly with significant loss in hardness, the DVS % MC increases are larger at the same %RH values, especially apparent for the Powdered material. The difference in % MC increases was attributed to difference in the operating principles of the two
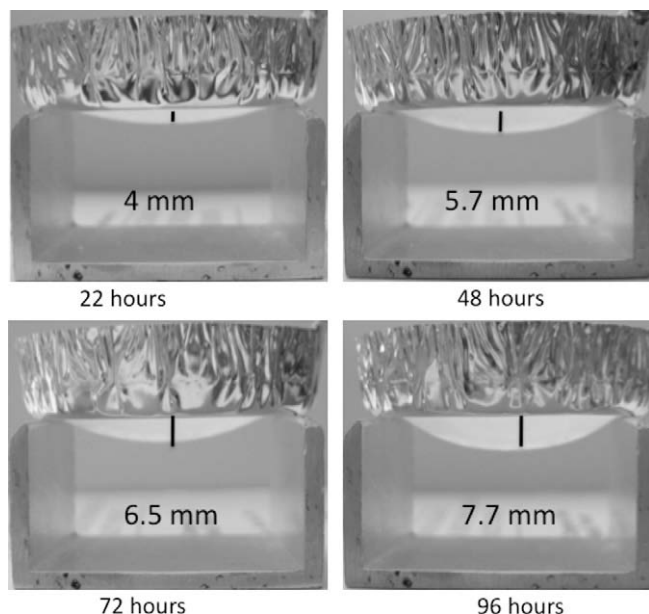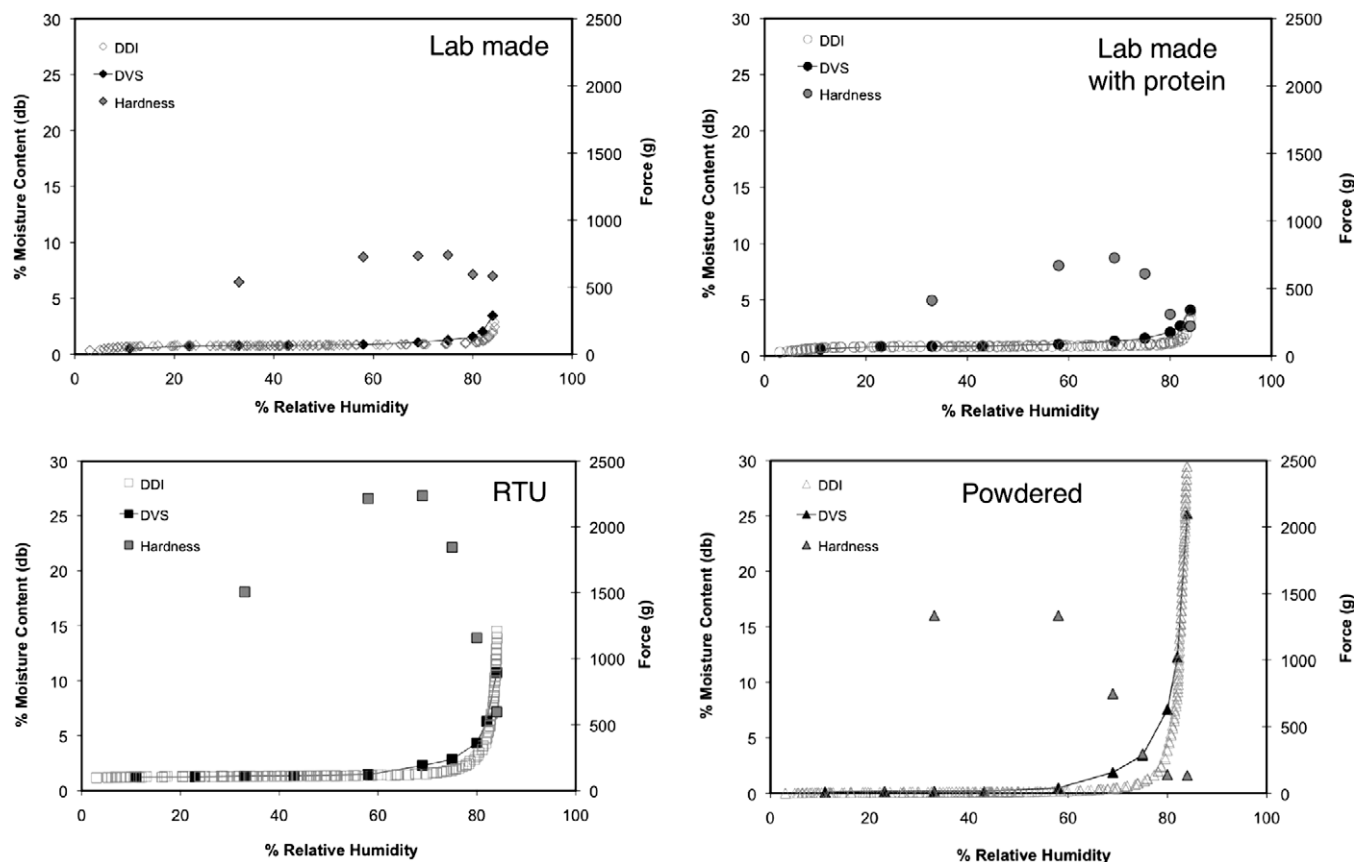
Fig. 5. DVS and DDI water vapour sorption isotherms and effect of increasing %RH on the hardness of the four gum paste materials stored at 25 °C. Notes: DDI duplicates are graphed, since each run is unique. Also, a line was used to connect the DVS points to further distinguish them from the DDI points.

methods. In the DVS method, the sample remains at each designated %RH until the sample attains a steady state moisture content; whereas in the DDI method, the moisture content is increased by exposing the sample to a small amount of water-saturated air (determined by the user via the flow rate), with subsequent measurement of sample a_w. The difference in operation between the two isotherm methods offers the opportunity to examine the sorption kinetics of materials.

The relationship between water sorption isotherm behaviour (DDI isotherms only) and hardness at 40 °C were also examined for each gum paste material (data not shown). Similar to the trends observed at 25 °C, the statistically significant decrease in hardness for the lab-made with protein, RTU, and Powdered materials occurred concomitantly with the initial stages of increased water sorption associated with the deliquescence of the crystalline sugar(s) present, with the deliquescence points being lower at 40 °C compared to 25 °C. Hardness for the lab-made gum paste was also not statistically different as a function of %RH at 40 °C; however, hardness was beginning to decrease at the high %RH values and would most likely become statistically significant if the storage %RH value was increased slightly, again similar to the observation made at 25 °C.

4. Conclusions

DVS and DDI water vapour sorption isotherms and textural properties (hardness, distance to break, and sag) were determined for four gum paste materials, two lab made gum paste materials (with and without egg protein) and two commercial gum paste materials (Ready-To-Use and Powdered mix). The physical state of all four gum paste materials, as evidenced by their type III iso-

therm shape and associated deliquescent behaviour, was nearly crystalline. Although, the major gum paste ingredient, powdered confectioner's sugar (sucrose), contained a small amount of amorphous sucrose (formed during the milling stage of sugar manufacturing), it was absent in the analysis of the finished gum paste. The difference in sorption behaviour and textural strength above 60% RH for the four gum paste materials at both 25 °C and 40 °C was driven mainly by the difference in deliquescence points between the materials, but was also influenced by the other gum paste ingredients. The lower deliquescence points (RH_o) obtained for the commercial gum paste materials (at both 25 °C [DVS and DDI] and 40 °C [DDI]) compared to the lab-made materials (with and without egg protein) were attributed to the presence of glucose (as dextrose, corn syrup or corn syrup solids), in addition to sucrose, in the two commercial materials. Although the inclusion of glucose in the commercial materials leads to decreased textural stability compared to the sucrose only containing lab-made materials, the glucose improves the workability of the gum paste. Decreased stability may be an acceptable trade-off for improved paste workability, especially if the finished gum paste product is unlikely to experience adverse %RH and/or temperature conditions. Additionally, commercial gum paste materials, such as those tested herein, provide a consistent and convenient gum paste product suitable for typical, short-term applications (i.e., edible wedding cake flowers).

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