

# State Diagram of Temperature vs Date Solids Obtained from the Mature Fruit

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Mature dates were dried achieving an increase in the level of solids from 70.8% to 92.4% (wet basis). Small deformation dynamic oscillation was employed to identify changes in the viscoelastic properties of dates as a function of solids. Samples were cooled or heated at a constant scan rate of 1 °C/min. At high temperatures, e.g., 70 °C, the storage and loss modulus ( $G'$  and  $G''$ , respectively) remained relatively independent of the time or frequency of observation, thus delineating the plateau zone. Cooling resulted in rapid development of both moduli with  $G''$  overtaking  $G'$ . This is known as the glass transition region and was used to define the rheological  $T_g$ . Eventually, the glassy state is reached where the storage modulus becomes dominant once more and approaches values of  $10^{9.5}$  Pa. The values of  $T_g$  were used to determine the metastable glass transition curve of mature dates. At lower levels of solids, i.e., between 11.7% and 64%, freezing experiments were employed to identify the equilibrium melting curve of ice. The state diagram yielded a maximally freeze-concentrated solute at 70% solids with the characteristic temperature of glass formation being  $-50$  °C. Data on equilibrium and kinetic events were modeled using the Chen and Gordon–Taylor equations yielding the rheological  $T_g$  for date solids at their effective molecular weight.

**Keywords:** State diagram; mature dates; freezing; rheological glass transition; drying

## INTRODUCTION

Dates, the fruit of the date palm *Phoenix dactylifera*, are one of the important agricultural commodities in the Middle East region. About 12 different varieties of dates are grown in Oman, and they constitute a significant source of nutrients for the inhabitants. In addition to their use as a dietary supplement, dates are of commercial importance and are traded or sold worldwide as a commodity or processed into various products (Omezzine et al., 1997). Following harvesting, dates are dried typically by air or solar methods to different levels of water for preservation. The water content of mature dates is about 30%, and drying can reduce it to less than 20%. At such high solids levels, the textural properties of dates should be determined by the transition from the rubbery to the glassy state observed as a function of temperature (White and Cakebread, 1966).

Glass formation is a second-order thermodynamic transition, generally characterized by a discontinuity in the physical, mechanical, electrical, and thermal properties of a material (Allen, 1993). Foodstuffs are rigid and brittle below the glass transition temperature. Nevertheless, they are not crystalline with a regular structure but retain the disorder of the liquid or amorphous state (Schenz, 1996). The physical state of foodstuffs is very stable below the glass transition temperature because compounds involved in deterioration reactions take many months or even years to diffuse over molecular distances and approach each other to react (Slade and Levine, 1991). Furthermore, water molecules become kinetically immobilized within the

concentrated phase, thus being unable to support or participate in these reactions (Mitchell, 1998).

Detailed reviews of the application of vitrification phenomena on the stability of biological materials have been prepared by Roos (1995) and Rahman (1999). Glassy and freezing characteristics of pure substances are more commonly reported than real foods, which are complex multicomponent mixtures (Rahman, 1995). However, the glass transition temperatures of freeze-dried strawberry and cabbage were measured as a function of water content by Roos (1987) and Paakkonen and Plit (1991), respectively, using differential scanning calorimetry. A basic understanding of physical properties in foodstuffs begins with the state diagram, which brings together a combination of equilibrium and metastable processes (Ablett et al., 1992).

In the present study, the state diagram of date solids obtained from the mature fruit was constructed using a combination of freezing experiments and dynamic oscillatory tests. It is hoped that successful application of the combined framework of the rheological glass transition temperature with freezing points to the structural properties of dates will guide application of the approach to real foods, thus facilitating rationalization of fundamentals and product development.

## MATERIALS AND METHODS

Mature dates of the Barni variety were harvested in September 1999 from date trees grown at the Agricultural Experiment Station of the Sultan Qaboos University and were stored at  $-20$  °C. The moisture content of the harvested dates was measured gravimetrically using an oven at 105 °C for at least 18 h of drying and was found to be  $29.2 \pm 0.3\%$ . The average length of the major and minor axis of mature dates is  $34 \pm 1$  and  $17 \pm 1$  mm, respectively. These were measured

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with a pair of dividers and recorded against a ruler. Average mass of the fruit is  $6.0 \pm 0.5$  g (Denver Instrument, XL-3100 balance) with 96% carbohydrates. Reduced sugars constitute a 50:50 mixture of glucose and fructose at a total level of solids of 92%. Unreduced carbohydrates include starch and pectin at 1.1% and 0.9%, respectively.

The dates were removed from the store and placed on a wire mesh tray as a layer. The samples were then dried in a convection air-dryer at 70 °C, with the relative humidity being 3.6%. Samples were taken out from the drier at different time intervals (0–7 day) and kept at 4 °C for more than 24 h in air-sealed polyethylene bags to equilibrate the moisture profile.

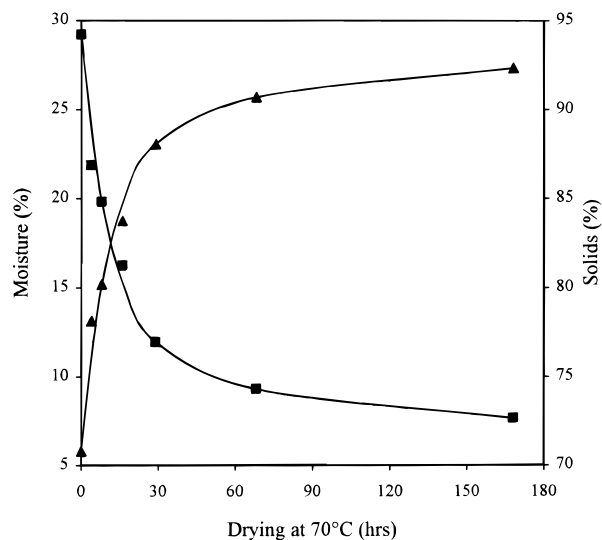
Rheological tests under low-amplitude oscillatory shear were performed using the Advanced Rheometrics Expansion System (ARES), which is a controlled strain rheometer (Rheometric Scientific, Piscataway, NJ). ARES has an air-lubricated and essentially noncompliant force rebalance transducer with the torque range being between 0.02 and 2000 g cm<sup>-1</sup>. This facilitates accurate recording of values in high modulus glass systems. For precise control of sample temperature, an air convection oven was used that has a dual-element heater/cooler with counter-rotating air flow covering a wide temperature range (-60 to 130 °C). This allowed recording of the viscoelastic properties of dates deep into the glassy state. In doing so, the parallel-plate geometry was preferred with the diameter of the top plate being 5 mm. The measuring gap between the plates was fixed at 3 mm. Samples were loaded onto the preheated platen of the rheometer (typically at 70 °C) and cooled at a scan rate of 1 °C/min. Heating runs at the same scan rate were interrupted periodically by frequency sweeps (0.01–100 rad/s).

Cooling curves during freezing of the dates were obtained using a programmable freezer at a scan rate of 1 °C/min (as for the rheology experiments). The freezing point is pinpointed at the onset of a relatively long temperature plateau that follows supercooling of the sample on a plot of time vs temperature. Details on the derivation of the cooling curves for foodstuffs are given in Rahman (1995). Dates were homogenized with the required amount of distilled water and left to equilibrate for 24 h in air-sealed containers at 4 °C. Samples filled a metallic cylinder, which was placed in the freezer. During experimentation, the temperature change as a function of time was logged by an automatic thermocouple positioned deep into the sample. For both rheological and freezing experiments, selected samples were run twice unveiling overlapping mechanical spectra and cooling curves.

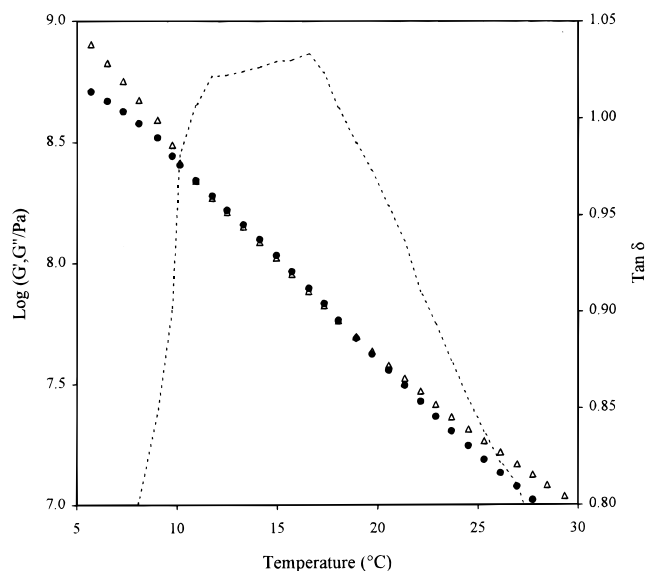
## RESULTS AND DISCUSSION

**Rheological Approach in the Description of Vitrification Phenomena in Foodstuffs.** A state diagram in its simplest form represents the pattern of change in the physical state of a material as a function of increasing levels of solids (Roos and Karel, 1991). On the basis of the moisture content of mature dates (29.2%), water was removed or added to prepare compositions with a level of solids ranging from 11.7% to 92.4%. Figure 1 reproduces the reverse relationship between moisture content and level of solids with increasing duration of drying at 70 °C. There is a rapid loss of water with up to 30 h drying whereas further treatment produces dates with the moisture content approaching asymptotically a constant value. Most of the remaining water is believed to be tightly bound to the solids (about 5%), often referred to as an adsorbed monomolecular layer of water (Potter, 1986).

Oscillatory measurements are now established as a productive line of attack for the development of structure–function relationships in food products (Richardson and Kasapis, 1998). Dynamic oscillation is capable of resolving the liquid-like (viscous) and solid-like (elastic) response of dates to imposed deformation



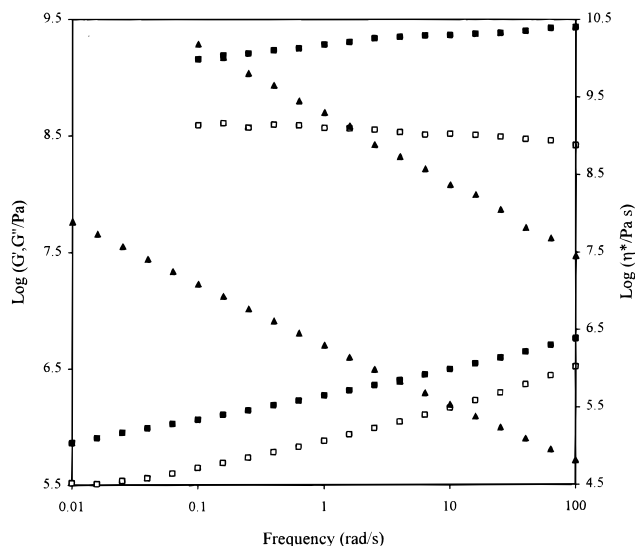
**Figure 1.** Effect of drying at 70 °C on the moisture content (■) and level of solids (▲) of mature dates.



**Figure 2.** Development of  $G'$  (▲),  $G''$  (●), and  $\tan \delta$  (---) as a function of temperature for a date sample with 90.7% solids (frequency: 1 rad/s; strain: 0.05%).

(Figure 2). Viscous and elastic responses can therefore be characterized independently and quantified as the storage and loss moduli ( $G'$  and  $G''$ , respectively). Figure 2 also depicts the tangent of the phase-lag ( $\delta$ ) between deformation and resistance, which provides a convenient index of the proportion of the liquid-like character in dates at each stage of drying:  $\tan \delta = G''/G'$ .

At the upper range of temperature,  $G'$  dominates  $G''$  with values at 28 °C being 13.5 and 10.2 MPa, respectively. Moduli converge at lower temperatures and the overall response becomes liquid-like (i.e.,  $G'' > G'$ ). The transformation in structural properties is also seen in the temperature dependence of  $\tan \delta$  that diverges from well below 1 to 1.035 at 16.5 °C. This is very different from the thermal profile of aqueous polysaccharide or gelatin samples that remain liquid-like at high temperatures ( $\tan \delta > 1$ ). Cooling of the solution induces a coil-to-helix transition leading to the formation of cohesive networks with  $\tan \delta$  values as low as 0.01 (Papageorgiou et al., 1994; Kasapis et al., 1993).

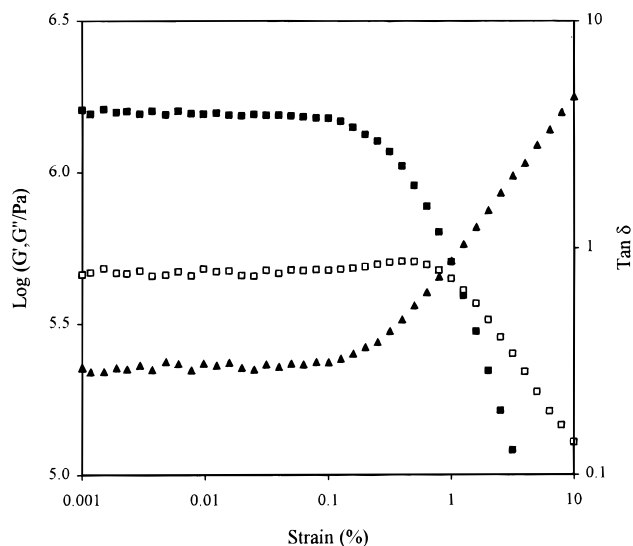


**Figure 3.** Frequency dependence of  $G'$  (■),  $G''$  (□), and  $\eta^*$  (▲) for date samples with 92.4% (bottom spectrum) and 83.8% solids (top spectrum). The frequency sweeps were taken at 70 and  $-35$  °C, respectively (strain: 0.05%).

The elastic-to-viscous transformation observed in Figure 2 is also seen in the cooling profiles of amorphous synthetic polymers and high sugar/biopolymer mixtures. In those cases, the characteristic feature of structural properties at high temperature is the so-called "plateau zone", which is recorded as a function of frequency of measurement (Ferry, 1980a; Evageliou et al., 1998). Figure 2 illustrates the viscoelastic properties of dates at a single frequency, namely, 1 rad/s; but configurational rearrangements as a function of time are ascertained in the form of a frequency sweep: in this context, time (s) = 1/frequency (Hz). Dates are high sugar biopolymer mixtures, and implementation of a frequency sweep at 70 °C unveils a typical plateau zone with a dominant elastic profile ( $G' > G''$  between 0.01 and 100 rad/s in the bottom spectrum of Figure 3).

According to Ferry (1980a), viscoelastic functions in a mechanical spectrum relate to configurational rearrangements between macromolecular entanglements and beyond entanglements (short and long relaxation times, respectively). The former is critical in vitrification phenomena whereas the latter determines the flow properties of the material. The plateau zone lies in the intermediate time scale of observation; hence, neither process contributes significantly to relaxation. As a result, the traces of shear modulus in Figure 3 are relatively independent of frequency but show a slight minimum of  $G''$  as the flow region is approached below 0.01 rad/s.

We have also examined the mechanical properties of the plateau zone as a function of increasing amplitude of oscillation. In doing so, the frequency of oscillation was kept constant at 1 rad/s, but the applied strain increased from 0.001 to 10% (Figure 4). The values of shear modulus remain constant up to 0.1% strain, which demarcates the limits of the linear viscoelastic region. The experimental strain of the present study is 0.05% and, therefore, lies well within this region. At higher levels of deformation, however, the network breaks down with concomitant drop in the values of storage modulus. At that stage, the viscous resistance shows a rise and subsequent drop ( $\sim 0.5\%$  strain), which may be attributed to fragments of the broken network confer-



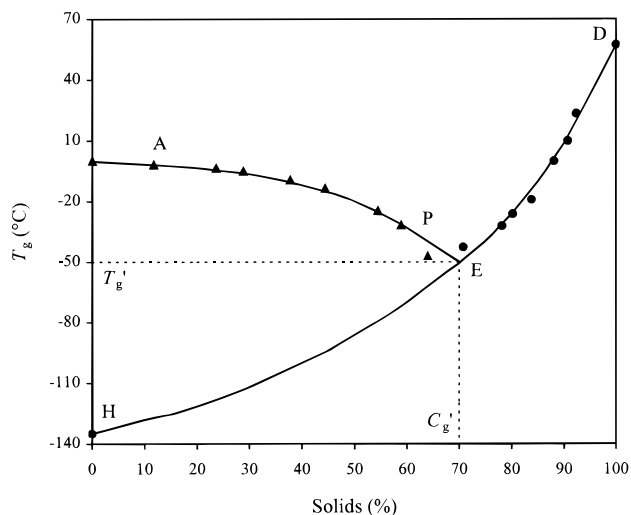
**Figure 4.** Strain sweep of  $G'$  (■),  $G''$  (□), and  $\tan \delta$  (▲) at 40 °C for a date sample with a solids content of 83.8% (frequency: 1 rad/s).

ring a viscosity contribution before the inevitable decrease as they are broken down further. Similar profiles of large deformation analysis have been recorded for a number of food materials including soybean, milk protein, and pumpkin pectin (Chronakis and Kasapis, 1993; Ptitchkina et al., 1994). Eventually, the trace of  $G'$  overtakes that of  $G''$  with the values of  $\tan \delta$  increasing rapidly above 1. At the upper range of deformation, date ingredients flow freely, and the strain sweep now becomes the mechanical analogue of network melting during heating.

Cooling the dates from 70 °C results in change from the plateau zone to the glass transition region. Here the thermal motions are oblivious to the topological restraints imposed by entanglements and contribute mainly to an energy dissipation process. This is shown in Figure 2 in the form of a disproportionate increase in the values of loss modulus, which become higher than those of storage modulus. Eventually, the system enters the glassy state where only stretching and bending of chemical bonds is permitted (Ferry, 1980a). The slight motions contribute mainly to the elastic component of the network, which dominates the oscillatory readings once more. In Figure 2, this occurs at temperatures below 10 °C, and it is accompanied by a drop in the values of  $\tan \delta$  below 1.

Formation of the glassy state results in a significant arrest of translational molecular motions with materials becoming extremely rigid. The top spectrum in Figure 3 reproduces the rheological glassy state of dates obtained at  $-35$  °C. Neither modulus shows a significant frequency dependence, and values of the solid-like response approach  $10^{9.5}$  Pa at 100 rad/s. The rigidity of the glassy state stands almost 4 orders of magnitude above the recorded values for the plateau zone of dates. Similar data have been reported for the glassy state of polyisobutylene (Ferry et al., 1953) and recently for the high sugar mixtures of gelatin (Kasapis et al., 1999).

**Use of the Rheological Glass Transition Temperature in the Construction of a State Diagram.** The dependence of viscosity on temperature has been used in the past to estimate the glass transition temperature ( $T_g$ ) of materials. In doing so, it was assumed that the viscosity at  $T_g$  was  $10^{12}$  Pa s $^{-1}$ . We were unable

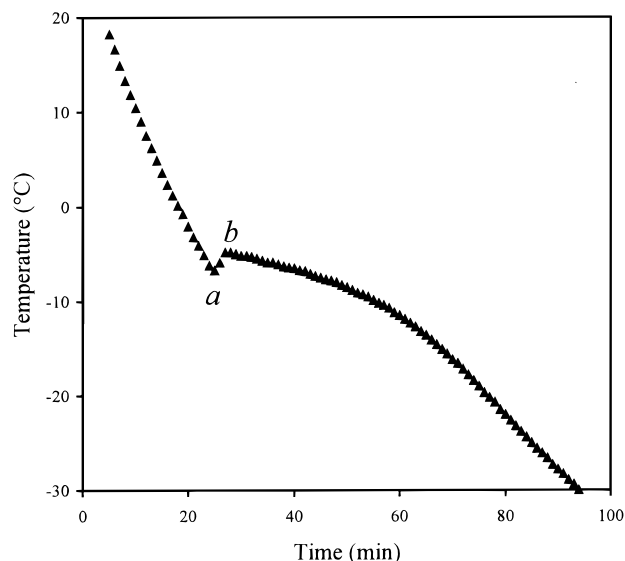


**Figure 5.** State diagram of temperature vs percentage solids obtained from mature dates incorporating the curve of the rheological glass transition temperature (●) and the freezing curve (▲).

to find hard experimental evidence to substantiate this value of viscosity or its shear-rate dependence at the glassy state. In practice, experimental viscosity values do not exceed  $10^{6.5}$  Pa s<sup>-1</sup>, and a long extrapolation to  $10^{12}$  Pa s is implemented in an attempt to predict the  $T_g$  (Noel et al., 1991; Angell, 1988). However, results reproduced in Figure 3 demonstrate the shear-thinning nature of complex viscosity ( $\eta^*$ ) at the plateau zone and the glassy state in mature dates. Within the accessible range of observation, log complex viscosity versus log frequency descends steeply over 3 orders of magnitude with a slope not far from  $-1$ . Thus, the absence of “leveling off” in the trace of  $\eta^*$  makes predictions of  $T_g$  rather tenuous.

Research in amorphous synthetic polymers and diluted systems describes the temperature dependence of molecular processes by means of measurements of shear moduli within the linear viscoelastic region. The  $T_g$  is pinpointed as the threshold of the glass transition where molecular adjustments take place within the experimental time scale and the glassy state where thermal motions can no longer occur within the experimental settings (Ferry, 1980b). For the date sample with a solids content of 90.7%, this change in state is reflected in the transformation from viscous to elastic phenomena at about  $10^{8.5}$  Pa, a result that makes  $T_g$  equal to 10 °C (Figure 2). The approach will now be followed to construct the state diagram of temperature versus solids for mature dates.

Figure 5 reproduces the  $T_g$  data for seven samples of mature dates covering a solids content between 70.8% and 92.4%. Together with the  $T_g$  of pure water [estimated at  $-135$  °C in Johari et al. (1987)] and the prediction of the Gordon–Taylor equation for the  $T_g$  of date solids (see below), they define the glass transition curve (DEH in Figure 5). The curve is considered to reflect metastable or kinetic events since its precise position is a direct outcome of the cooling regime. As far as we are aware, this is the first state diagram incorporating a glass transition curve from rotational dynamic oscillation. Preparations with a level of solids below 70% develop crystallinity, which reduces the adhesion with the measuring plate, thus making samples prone to slippage. Within this region, freezing experi-



**Figure 6.** Cooling curve of date solids at 71.2% water content featuring the onset of ice crystallization (a) and the equilibrium freezing point (b).

ments were preferred to provide information on the first-order thermodynamic transitions in date preparations (i.e., the formation of ice).

As illustrated in Figure 6, the transition temperature for freezing was determined as the onset of the observed change in the cooling curve of dates. Cooling below the initial freezing point of a sample without formation of ice is defined as supercooling. Following initial supercooling, the critical mass of nuclei is reached with the system nucleating at point (a). At this stage, the sample releases its latent heat of fusion faster than the amount of heat removed from the system causing an instantaneous increase in temperature to the equilibrium freezing point (b). Figure 5 shows the temperatures at point (b) recorded from cooling curves. The range of solids covered was from 11.7% to 64% (points A and P, respectively), thus delineating the freezing curve,  $T_F$ . Curve AP represents equilibria between the solution and the solids formed, and it has a negative gradient showing the expected decrease in the freezing point with increasing concentration of solids.

The intersection of the equilibrium and kinetic events is at  $\sim 70\%$  solids (point E in Figure 5), which represents the maximally freeze concentrated solute. At this stage, the concentrated solutes in dates become so viscous that no more ice will crystallize and the system passes through the glass transition curve at  $T_g'$ , which is about  $-50$  °C. Thus, the characteristic temperature of glass formation ( $T_g'$ ) is lower than the eutectic point used to denote the temperature of solvent crystallization. The water content at point E is known as the unfreezable water, which for dates is  $\sim 30\%$  ( $C_g'$ ). State diagram studies of sucrose and fructose produced unfreezable water values between 20 and 21% (Roos and Karel, 1991; Ablett et al., 1992, 1993). Furthermore, the content of unfrozen water was 21.4% for strawberry and within the range of 26.3–30.4% for cabbage (Roos, 1987; Paakkonen and Plit, 1991). The higher levels of unfreezable water in foodstuffs should reflect the presence of biopolymers whose long chains contribute considerably to the immobility of water molecules in the system.

**Completion of the State Diagram of Date Solids Using Empirical Modeling.** In 1952, Gordon and

Taylor proposed an empirical equation to predict the glass transition temperature of mixtures comprising amorphous synthetic polymers. Today, this is commonly used to predict the vitrification properties of foodstuffs and biological materials:

$$T_{gm} = \frac{X_s T_{gs} + kX_w T_{gw}}{X_s + kX_w}$$

where  $T_{gm}$ ,  $T_{gs}$ , and  $T_{gw}$  are the glass transition temperatures of the mixture, solids, and water, respectively. Similar notations are used for the weight fractions of constituent ingredients ( $X_s$  and  $X_w$ ).  $k$  is the Gordon–Taylor parameter, which from the thermodynamic standpoint is equivalent to the ratio of the change of component mixture specific heat at their  $T_g$  (Couchman and Karasz, 1978). The Gordon–Taylor equation can be recast in a linear form assuming that the weight fraction of the water molecules is negligible in date samples subjected to prolonged drying. Thus, the intercept and the gradient of the linearized form of the equation afford estimation of the  $T_{gs}$  and  $k$ , respectively. Considering that the glass transition temperature of supercooled water is  $-135\text{ }^\circ\text{C}$ , the values of  $T_{gs}$  and  $k$  for dates were found to be  $57.4\text{ }^\circ\text{C}$  and  $3.2$ , respectively. The  $T_{gs}$  corresponds to point D in Figure 5. This appears to be a reasonable estimate, taking into account that the  $T_{gs}$  values of fructose and glucose are  $5$  and  $31\text{ }^\circ\text{C}$ , respectively, and those of pectin and starch are in excess of  $100\text{ }^\circ\text{C}$  (Roos and Karel, 1993). Furthermore, the predicted value of  $k$  is congruent with those in the literature for strawberries and horseradish [ $4.7$  and  $5.3$  in Roos (1993)].

Dates, as most of foodstuffs, are mixtures of several components; therefore, the state diagram amounts to an average measure of their functional properties in the fruit. Along these lines, estimation of the effective molecular weight of the date solids is appropriate, since it quantifies the driving force behind the interplay of crystallization–vitrification phenomena in the system. The origins of this calculation emanate from the Clausias–Clapeyron equation, which follows from the first and second law of thermodynamics (Atkins, 1984). The equation can follow the depression of the freezing point of a sample at very dilute concentrations of dissolved solids. In high solids systems, the concept of nonsolvent-bound water becomes important and requires a modification in the Clausias–Clapeyron equation. Thus, the expression proposed by Chen (1986) incorporates the concept of unfreezable water in the following form:

$$\lambda_s = \frac{\beta X_s}{(1 - X_s - BX_s)\Delta}$$

where  $\Delta$  is the freezing point depression ( $T_{\text{water}} - T_{\text{food}}$ ),  $\beta$  is the molar freezing point constant of water ( $1860\text{ kg K}^{-1}/\text{kg mol}^{-1}$ ), and  $X_s$  is the mass fraction of solids in the sample.  $B$  is the amount of unfrozen water bound per unit weight of solids that remains unavailable for freezing regardless of temperature. The value of  $B$  for mature dates is obtained from the experimental data of Figure 5, thus being  $0.429\text{ kg of water/kg of solids}$  (point E). Application of this approach to the data of the freezing curve in Figure 5 yields a value for the effective molecular weight,  $\lambda_s$ , of date solids of  $200 \pm 10$ . As in the case of the glass transition temperature of date solids, the prediction of  $\lambda_s$  is higher than the

molecular weight of glucose or fructose, thus reflecting the contribution of the polymeric material to the cryohydric properties of the fruit.

## CONCLUSIONS

Dates are increasingly enjoyed for their gourmet taste and remain one of the staples in the diet of the peoples of the Arabic Region. There is, however, scanty information in the literature on the structural properties of date ingredients in relation to the temperature of processing and level of addition to product formulations. Clearly successful use of date ingredients (syrup, pectin, fiber) in the development of novel appealing formulations and the replacement of conventional ingredients (e.g., gelatin, which has fallen out of fashion because of vegetarianism; BSE scare; and religion) will confer substantial wealth to cultivators and manufacturers alike.

The present investigation attempts to map out the liquid, rubbery, glassy, and crystalline consistencies of date solids by means of a state diagram. In doing so, it utilizes the freezing point curve in combination with the recently introduced concept of the rheological glass transition temperature. The latter was defined as the cross over of storage and loss moduli at the conjunction of the glass transition region and the glassy state. At this point, the shear moduli achieve values of  $10^{8.5}\text{ Pa}$ . It is hoped that the rheological approach will be of use in the elucidation of the structural properties of purified date ingredients and other foodstuffs.

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Received for review December 14, 1999. Revised manuscript received May 11, 2000. Accepted May 11, 2000.

JF9913615