Definition of a Mechanical Glass Transition Temperature for Dehydrated Foods

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A new concept of the mechanical glass transition temperature (T_g) is presented with application in dehydrated high-sugar/gelatin mixtures, fish, and fruits. The macroscopic basis and manner of relaxation processes during vitrification of these foodstuffs are developed using small deformation dynamic oscillation, the master curve of viscoelasticity, and the time−temperature superposition principle. The quantitative features of the mechanical T_g are based on the combined framework of free volume/WLF theory and the Andrade equation. It is proposed that the thermal profile of storage modulus on shear is a fundamental index of monitoring changes in a glassy structure, and several cases are presented in support of this concept.

INTRODUCTION

There is now extensive literature on the concerns and applications of the amorphous state of materials with emphasis on food-related and pharmaceutical products (*1*). Early events in the development of a real understanding in the field focused on the interrelationship between molecular mobility and the diffusion-limited properties of materials containing amorphous regions (*2*, *3*). Critical questions raised included the effect of molecular structure and network morphology on vitrification phenomena, the choice of the most appropriate experimental techniques for their identification, the rates of enzymatic and chemical reactivity below the glass transition temperature (T_g), and the functionality of carbohydrates as stabilizers of labile biological materials (*4*−*8*).

Thirty years later, there is a good understanding of the implications of material polyamorphism and/or heterogeneity on the physicochemical stability of pharmaceuticals (*9*). The difficulty of modeling the distribution of relaxation processes in phase-separated/complex mixtures of drug matrices is acknowledged. This issue may be tackled in the future via the introduction of the concept of mobility transition temperatures of residual water below the T_g (*10*). Further research in drug manufacture will have to deal with the importance of glass density and the specific interactions between reactant and glassy solid in the stability of preparations (*11*).

In food-related applications, there is an extensive development of empirical and theoretical approaches in an attempt to bring the sophisticated "synthetic polymer approach" to biological materials (*12*−*14*). The primary concern of the approach is to give a reliable estimate of the values of glass transition temperature in relatively simple model systems and composite foods. In doing so, the standard techniques of differential

scanning calorimetry (DSC) in plain and modulated modes, nuclear magnetic and electron spin resonance spectroscopies (NMR/ESR), and dynamic mechanical thermal analysis (DMTA) are largely employed (*15*, *16*). As far as mechanical measurements go, the myths of T_g pinpointed at the maximum of the loss modulus trace, of the equivalence between the DSC T_g and the DMTA T_g obtained at 0.001 Hz, and of the universal WLF constants are hard to beat (*17*, *18*).

In terms of food processing and storage, interesting examples related to vitrification phenomena include the association between molecular mobility and textural properties during aging of starchy formulations (*19*, *20*), the effect of molecular structure on the functional stability of proteins (e.g., hydrolyzed soy), the relevance of sugar state diagrams to ice cream technology (*21*, *22*), and the dehydration/preservation of fruits, vegetables, and meat or fish in relation to the product quality. Food dehydration increases dramatically the concentration of solids in the remaining water, thus bringing the system close to its rubber-to-glass transition (*23*, *24*). This, of course, greatly effects the textural properties of dried foodstuffs, and the aim of the present paper is to offer insights into the problem of developing a glass transition temperature as a means of controlling the mechanical properties of these systems.

EXPERIMENTAL PROCEDURES

Materials. Fresh abalone was obtained from the fish market, iced, and brought chilled into the laboratory. The mass and size of the abalone were 100 g and 8.5 cm diameter, respectively. The abalone was washed, frozen at −40 °C for at least 48 h, and placed in an automatically controlled freeze-dryer (VirTis SP Industries Co., Gardiner, NY). The plate temperature was set at −20 °C with a vacuum of 800 mTorr (108 Pa) in the chamber while the condensing plate temperature was set at −65 °C. At the end of 72 h of drying, the moisture content was ~4% (wet basis). The moisture content of the samples was modified by placing them in separate open weighing bottles and storing in air-sealed glass jars.

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Table 1. Data on the Physicochemical Characterization of Our Gelatin Sample

sample	ps4	sample	ps4
bloom[a]	48	tetra + penta	2.36
isoelectric point (pI)	8.7	γ	3.06
% moisture (wwb)	13.5	β	8.59
calcium (ppm)	160	α	11.39
sulfate (%)	1.48	subunits 1	9.43
chloride (%)	0.54	subunits 2	15.14
phosphate (ppm)	18400	subunits 3	14.70
M_n[b]	29200	subunits 4	33.46
mol wt > 10^6 kDa	0.56		
mol wt > 540 kDa	1.63		

[a] Bloom is the weight in grams required to push a piston of strictly defined shape 4 mm into a gelatin gel matured for 16–18 h at 10 °C. [b] The α, β, and γ fractions of gelatin are well characterized and monodisperse with characteristic masses. The latter two are, respectively, a dimer and a trimer of the α fraction. The tetra and penta are higher order but less well-defined fractions. The low molecular weight side of the GPC spectrum is divided arbitrarily into four different fractions of subunits. The percent weight of the GPC spectrum in each of the 10 molecular mass classes is quoted.

The jars reached equilibrium relative humidity with saturated salt solutions or under conditions of high relative humidity atmosphere (*25*). A test tube containing thymol to prevent mold growth during storage was also added. Twice per week, the samples were removed and weighed until the mass loss or gain reached ≤0.001 g for successive weighings. Equilibrium was reached within 6–8 weeks depending upon the water activity of the sample. The equilibrium moisture content of the sample was measured gravimetrically by drying in an oven at 105 °C for at least 24 h to determine the solid mass in the sample.

Whole fresh long-tail tuna (*Thunnus tongol*) was also purchased from the local fish market. The mass and length of the whole fish were from 2.3 to 2.6 kg and from 0.60 to 0.65 m, respectively. The whole tuna was washed with tap water and filleted with a sharp knife. A portion of the red meat was removed from the fillets, and strips were prepared having 14 cm length, 3 cm width, and 1.5 cm thickness, respectively. The strips of tuna were frozen and freeze-dried, and the moisture content was manipulated along the lines described for abalone.

Dried apples, pears, apricots, plums, and dates were purchased from a local supermarket, and they were stored in sealed containers for a week at 4 °C before being used for experiments. Fruits were taken from the cool room, and cylinders of 5–10 mm thickness and 20–30 mm diameter were cut carefully using a sharp knife and a cork borer for rheological investigation. The moisture content of the samples was determined as described in the preceding paragraphs.

The gelatin sample (ps4) was a gift from Sanofi Bio-Industries, Baupte, Carentan, France. It was extracted from a single batch of pigskin produced by acidic hydrolysis of collagen (type A). The isoelectric point of the gelatin fraction was close to that of the parent collagen (pH 9.4). This and other analytical characteristics of the sample were determined by the manufacturer and are given in **Table 1**. The bloom value is proportional to the elastic modulus of the gelatin gel, and it decreases with decreasing molecular weight.

Sucrose was of AnalaR grade from Sigma. The glucose syrup used was a product of Cerestar, Vilvoorde, Belgium. The dextrose equivalent of the sample was ~42. The total level of solids provided by the manufacturer and confirmed by refractometry was 83%, and glucose syrup compositions in this work refer to dry solids. Gel permeation chromatography data showed an extensive degree of polydispersity, which at 83% solids prevents crystallization of the material at subzero temperatures, as demonstrated by DSC and small deformation dynamic oscillation (*26*).

Rheological Methods. Dynamic oscillation routines have been used to demonstrate the development of structures having viscoelastic properties as a function of temperature or time/frequency of measurement that can be associated with vitrification phenomena in food systems (*27*). In doing so, samples were loaded onto the plate of the rheometer and maintained at low temperature (between 25 and 50 °C)
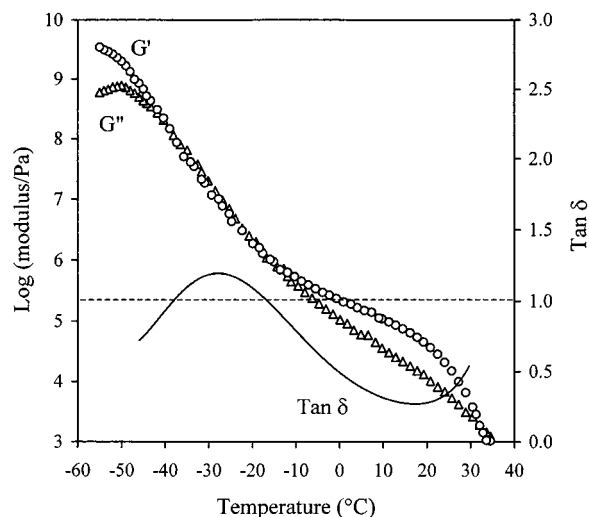

Figure 1. Cooling profiles of G' (○), G'' (△), and tan δ (—) for a mixture of 25% gelatin (ps4) with 40% sucrose + 15% glucose syrup obtained at a scan rate of 1 °C min^{-1} and frequency of 1 rad s^{-1}. The cooling and heating traces of the mixture in the glass transition region and the glassy state are superposable.

for a short time to reach thermal equilibrium. Then they were subjected to an oscillation on shear of set frequency (1 rad/s) and strain (from 2 to 0.00075%) while cooling at a rate of 1 °C/min to −70 °C. This was followed by a heating regimen to 40 °C using identical settings.

Readings of the rigidity/storage modulus (G'), viscous/loss modulus (G''), and dynamic viscosity (η^*) variation with temperature and frequency were obtained, and a measure of the "phase lag", δ (tan δ = G''/G'), gave an indication of the relative liquid-like and solid-like character of the material. Samples that showed an extensive transition from the rubbery to the glassy state were scanned down and then up once more, and mechanical spectra (from 0.1 to 100 rad/s) were monitored at regular temperature intervals (3–5 °C).

Measurements were performed on a commercial controlled strain rheometer, which employs an actuator to apply a deforming strain to the sample and a separate transducer to measure the resultant stress developed within the sample (Advanced Rheometric Expansion System of Rheometric Scientific, Piscataway, NJ). The high-resolution actuator has a low-end dynamic strain of 5 μrad. The transducer is essentially noncompliant and covers a torque range from 0.02 to 2000 g cm. During experimentation the torque varied accordingly to maintain a constant strain, which allowed recording of modulus values up to 10^{10} Pa. The measuring geometry used parallel plates of 7.9 mm diameter for the top fixture, with the measuring gap being 3–6 mm.

Control of the sample temperature was achieved by an air convection oven with counter-rotating air flow capable of spanning a wide temperature range (PGC, Polycold Systems International, San Rafael, CA). Profiles of shear moduli, obtained from the mechanical spectra, were superposed as a function of frequency for subsequent quantitative analysis using the principle of time–temperature superposition (TTS). Results are the average of two replicates, with the rubber-to-glass transition being readily reproducible within a 3% error margin as a function of temperature or time scale of measurement.

RESULTS AND DISCUSSION

Temperature Profile of the Mechanical Glass Transition Region. An obvious rheological procedure to obtain information on the structural properties of dehydrated foodstuffs would be to examine G' and G'' as a function of temperature at a constant frequency or time of measurement. This is illustrated in **Figure 1** for a preparation that finds application in confections (gummy bears, wine gums, etc.) in flavor encapsulation and the preservation of bioactive molecules in glassy matrices (*28*). The sample was made by mixing gelatin with sugar at intermediate levels
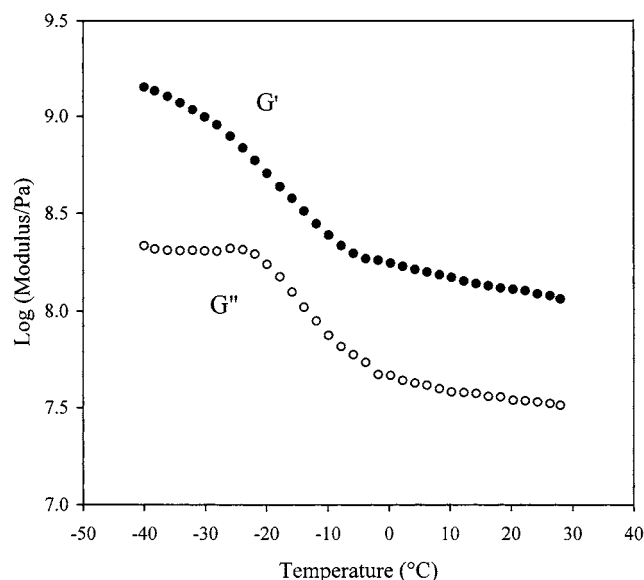
Figure 2. Heating profiles of storage (*G*′) and loss (*G*″) moduli for dried tuna at 70% solids: scan rate, 2 °C min^{-1}; frequency, 1 rad s^{-1}; strain, 0.005%.

of solids and then allowing gentle dehydration at 60 °C to yield a composition of 25% gelatin (ps4), 40% sucrose, and 15% glucose syrup.

A considerable part of the "master curve of viscoelasticity" has been captured within the experimentally accessible temperature range (*29*). At the upper range of temperature, the gelatin/cosolute mixture is a melt with the loss modulus dominating the storage modulus. Cooling brings about a rapid development in *G*′ with the two traces crossing over at a gelling point (∼31 °C), which demarcates the onset of the rubbery region. Mixtures are "true" gels with elastic consistency that can support their shape against gravity at ambient temperature. On further cooling (below −10 °C), the shear moduli develop rapidly and we consider values up to $10^{8.5}$ Pa. This is the glass transition region where transverse stringlike vibrations of polymeric chains diminish with reduced temperature (*30*). At the lowest temperature, there is yet another development, and a hard solid response is obtained (*G*′ values approach 10^{10} Pa). This is the fourth region of the master curve, the so-called glassy state, where in addition to stretching and bending of chemical bonds secondary mechanisms, for example, of pendant groups are ubiquitous (*31, 32*).

The gelatin/cosolute system exhibits classic viscoelastic behavior as pioneered by research in synthetic polymers (*33, 34*). The main features of the rubber-to-glass transition include a dominant viscous component (*G*″ > *G*′) and a spectacular dependence of viscoelastic functions on time or temperature. In **Figure 1**, the ratio of *G*″ to *G*′ (tan *δ*) between −17 and −39 °C acquires values >1 and, within the same temperature range, the increase in shear modulus is 3 orders of magnitude.

It appears, however, that the mechanical transition of dried fish and fruits is not that clearly defined. This is illustrated in **Figure 2** for the thermal profile of tuna meat dried to 70% solids. To start with, the magnitude of the plateau at temperatures >0 °C is unusually high, reaching values in excess of 10^8 Pa for the storage modulus. Second, the change in moduli at subzero temperatures is less than an order of magnitude from one step to another. Finally, the liquid-like response, which is the primary indication of glassy relaxation processes, is substantially diminished, with the values of tan *δ* throughout the experimental range remaining well below 1.

Delving into the synthetic polymer literature provides insights into the mechanism of this type of behavior. Thus, Favier et al. (*35*) prepared suspensions of ordered cellulose whiskers at a nanoscale size and mixed them homogeneously with a lattice of amorphous copolymerized styrene and butyl acrylate. Temperature profiles for the synthetic rubbery matrix at different contents of the rodlike cellulosic inclusions were recorded. There was a dramatic enhancement of network rigidity at the plateau of the high-temperature end with a concomitant reduction in the extent of the glass transition as the weight fraction of cellulose whiskers increased from 0 to 14%. A similar experiment was carried out on poly(ethylene terephthalate), a material that is amorphous when quenched from the melt but crystallizes partially during slow cooling (*36*). The effect of crystalline regions was a gradual transition of 1 order of magnitude, with the tan *δ* trace collapsing from a value of 3 to ∼0.2 as a function of the reduced cooling rate.

On the basis of this evidence, one envisages the mechanical profile of **Figure 2** as the outcome of a complex transformation occurring in a composite of amorphous and low-mobility regions. Clearly, drying of tuna meat produces tightly packed aggregates of reduced molecular mobility, an outcome that diminishes the opportunity for a full manifestation of the glass transition in these systems. In support of this, we were unable to obtain discernible glass transition spectra using the standard technique of modulated differential scanning calorimetry (MDSC) at various scan rates and annealing temperatures or times. In contrast, we were able to obtain and contrast T_g values from MDSC with the rheological T_g for mixtures of high sugar with gelatin or polysaccharide (*37, 38*).

Applying the Time−Temperature Superposition Principle to Dehydrated Biomaterials with Glassy Consistency. To circumvent the problem of a diminished glass transition in dehydrated fish and fruits and to identify an objective way to assess the temperature dependence of molecular processes in these systems, we opted to work from first principles. The thermal profiles discussed in **Figures 1** and **2** allow a first insight into the structural properties of materials. A more valuable find, however, allows complete dissociation of the contributions of temperature and frequency to the overall mechanical behavior according to the postulates of time−temperature superposition (TTS). The approach affords a device for changes in temperature to be seen as shifts in the frequency/time scale of mechanical spectra taken in a sequence of temperature intervals (*39*).

To demonstrate this in biomaterials, we cite frequency sweeps of the real and imaginary parts of the complex shear modulus, *G*′ and *G*″, for the ps4/cosolute mixture (**Figure 3**). Measurements were taken at 11 different temperatures between 14 and −55 °C and at 16 different frequencies from 0.1 to 100 rad s^{-1}. The modulus data covering the long time scales of the upper range of temperature remain relatively flat within the rubbery region, whereas further cooling brings about a rapid reinforcement of viscoelasticity, which unveils the glass transition region. At the low-temperature end of the experimental range, the values of *G*′ level off once more with a quantifiable endpoint (**Figure 3a**), thus unveiling the glassy state.

According to TTS, all measurements involve relaxation processes whether mechanical or electrical, and mathematically these can be analyzed in terms of a spectrum of relaxation times (*12, 40*). In a study of a large number of polymers, it was found that viscosity measured at a certain shear rate and temperature *T* is equivalent to viscosity measured at the product of the same shear rate times a scaling factor a_T (the so-called "shift factor") and the reference temperature T_0 (*41*). Therefore, for viscosities
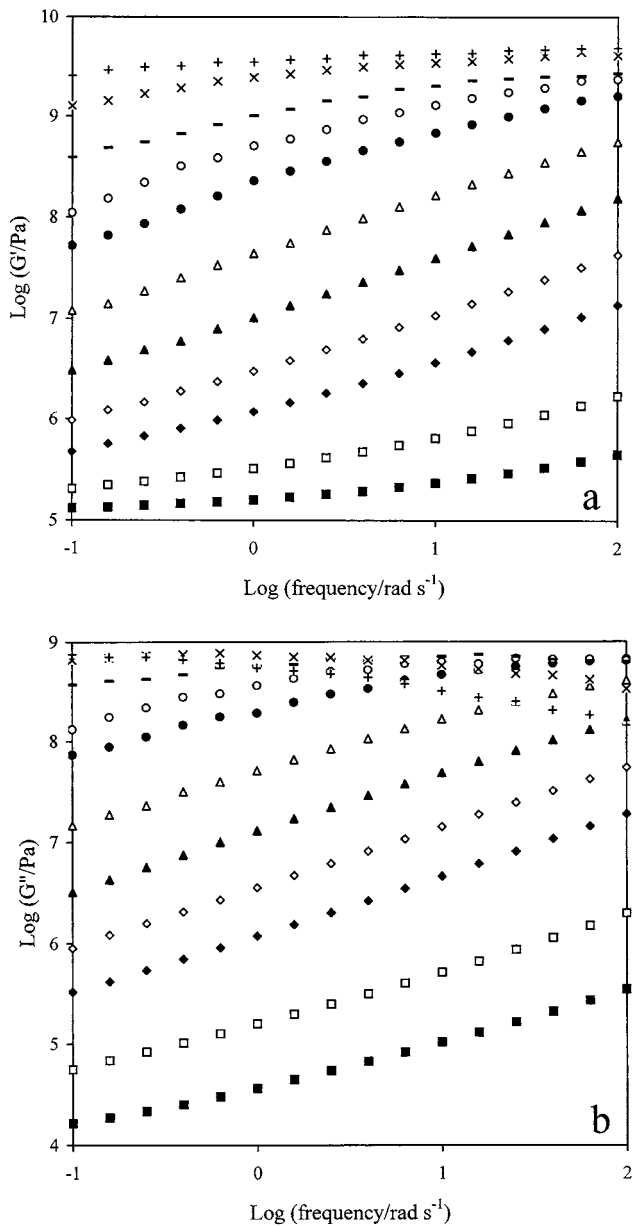
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Figure 3. Real (**a**) and imaginary (**b**) parts of the complex shear modulus, plotted logarithmically against frequency of oscillation for a sample of 25% ps4 with 40% sucrose and 15% glucose syrup. Bottom curve is taken at 14 °C (■); other curves successively upward, −1 (□), −16 (◆), −22 (◇), −28 (▲), −34 (△), −40 (●), −43 (○), −46 (−), −52 (×), and −55 (+) °C, respectively.

Figure 4. Master curve of reduced shear moduli (G'_p and G''_p) as a function of reduced frequency of oscillation (ωa_T) for a sample of 25% ps4 with 40% sucrose and 15% glucose syrup (reference temperature = −25 °C).

Figure 5. Temperature variation of the factor a_T within the glass transition region (■) and the glassy state (▲) for the mixture in **Figure 4**, with the solid lines reflecting the WLF and Andrade fits of the shift factors in the glass transition region and the glassy state, respectively (left *y*-axis), and first derivative plot of log G' (●) and log G'' (○) as a function of sample temperature, with the dashed line pinpointing the T_g prediction (right *y*-axis).

$a_T = \eta(T)/\eta(T_0)$. Of course, reduction of data to T_0 and the production of a single composite curve can be achieved for any modulus function: storage or loss modulus, $G'(\omega)$, $G''(\omega)$; stress relaxation modulus, $G(t)$, etc. Application of the approach to our materials produces modulus traces that are superposed horizontally along the abscissa at the reference temperature of −25 °C. This creates master curves of viscoelasticity, with the reduced variables, G'_p and G''_p, being plotted logarithmically in **Figure 4**.

Developing a Fundamental Indicator for the Glass Transition Temperature in Dehydrated Foodstuffs. To pinpoint the glass transition transition temperature, we use the premises of the free volume theory that has been widely employed in a quantitative fashion to interpret glassy phenomena in terms of molecular processes (*42*). According to the theory, T_g should be located
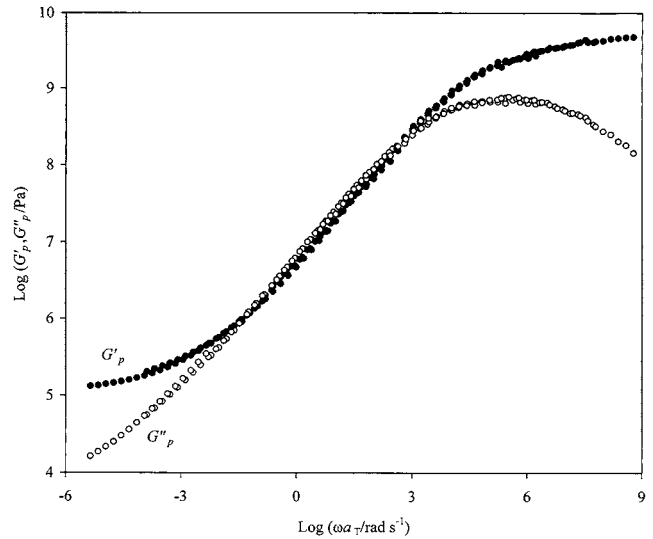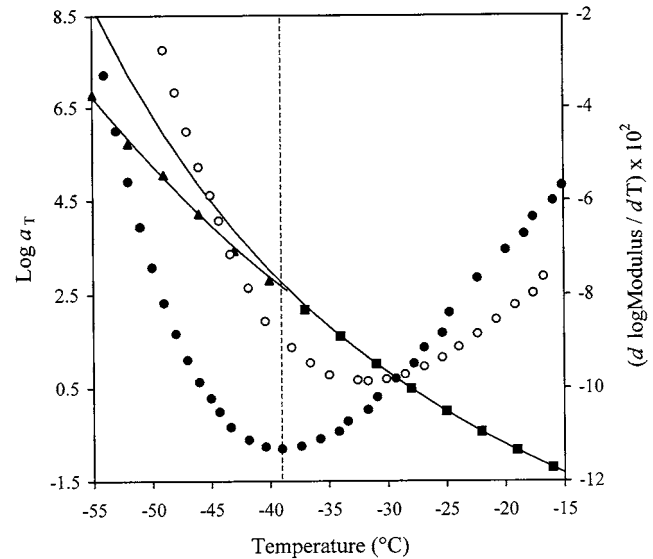
at the end of the glass transition region, where the free volume declines to insignificant levels [∼3% of the total volume of the material in Ward and Hadley (*36*)]. Gels and liquids at temperatures far above the vitrification point (i.e., at the onset of the glass transition or the rubbery region) have much higher free volumes, perhaps 30% instead of 3%.

According to the thermal profile in **Figure 1**, the glass transition region covers the temperature range of −17 to −39 °C, at which the values of tan δ remain >1. At lower temperatures (−40 to −55 °C), the solid-like response becomes dominant (tan δ < 1), an outcome that signifies the development of the glassy state. Thus, the conjunction of the glass transition region with the glassy state is clearly discernible, which pinpoints the experimental T_g of the ps4/sugar mixture at −39 °C.
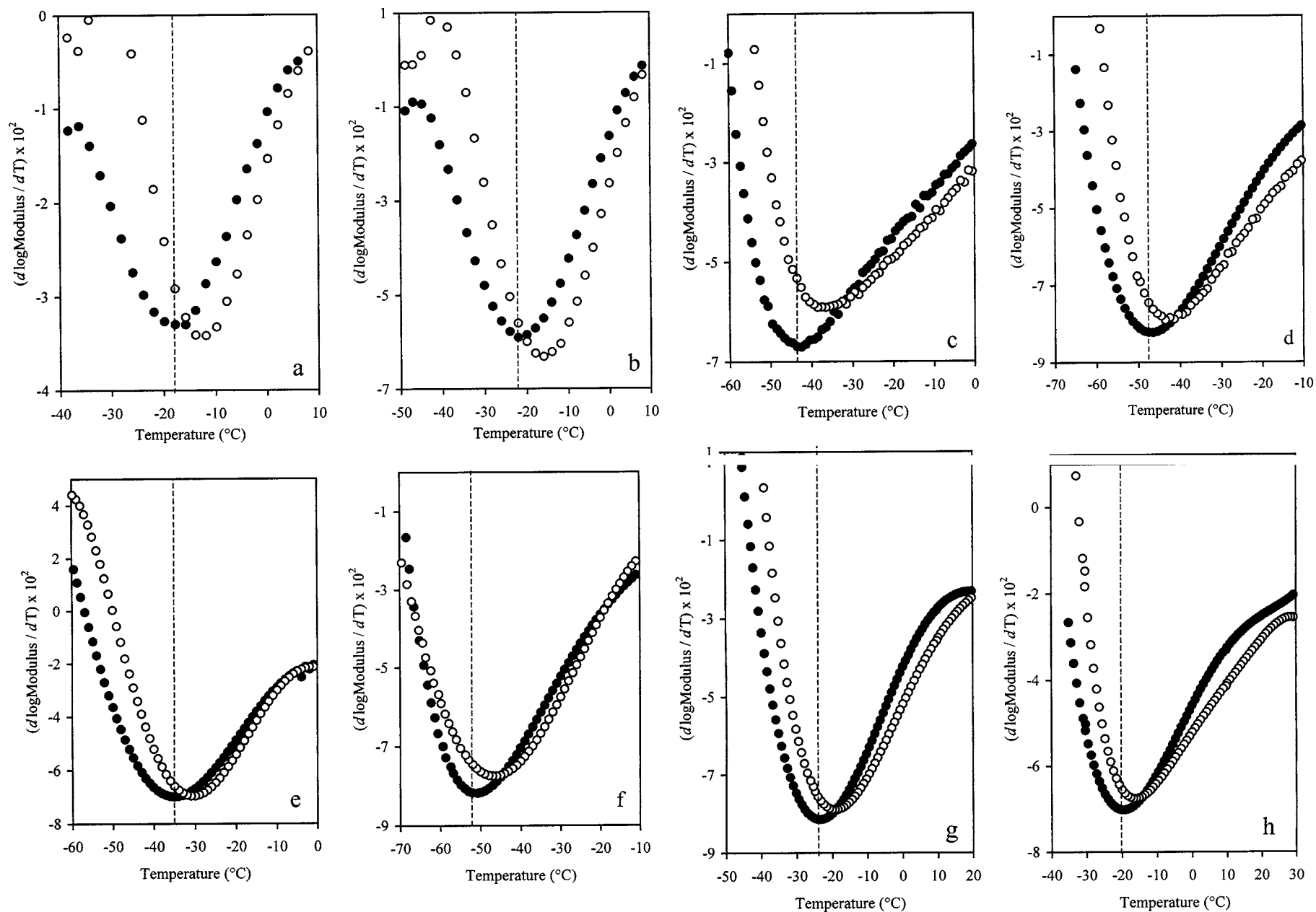
Figure 6. First-derivative plot of log G' (●) and log G'' (○) as a function of sample temperature plotted against temperature for (a) 70% tuna, (b) 70% abalone, (c) 67.2% apple, (d) 67% apricot, (e) 70.6% pear, (f) 60.9% plum, (g) 80.2% date, and (h) 83.8% date solids, respectively, with the dashed line pinpointing the T_g prediction.

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Experimental data can be compared with the predictions of the free volume theory epitomized in the Williams–Landel–Ferry (WLF) equation. This is an essentially empirical equation for the purpose of combining data derived at different temperatures into one master curve (*43*):

$$\ln [G(T)/G(T_0)] = \ln a_T = [-C_1(T - T_0)]/(C_2 + T - T_0)$$

T and T_0 are the experimental temperature and the reference temperature, respectively, and C_1 and C_2, the WLF constants, relate to the free volume, thus being particular to each preparation. Construction of the master curve in **Figure 4** entailed reduction of the frequency sweeps in **Figure 3**, thus yielding corresponding sets of shift factors. These are plotted for the ps4/cosolute mixture in **Figure 5**.

As shown, the WLF equation provides a good fit of the empirically derived shift factors in the glass transition region, which determine how much the frequency scale shifts with temperature. In addition to the glass transition region, the master curves in **Figure 4** cover the glassy state, where the values of G' approach a maximum and those of G'' decrease rapidly. The shift factors of mechanical spectra in the glassy state are reproduced in **Figure 5** and unveil a pattern of behavior that cannot be followed by the WLF equation. Instead, progress in mechanical properties at the region of the lowest temperatures is better described by the mathematical expression of Andrade (*44*):

$$\log a_T = \frac{E_a}{2.303R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

This yields the concept of activation energy (E_a) for an elementary flow process in the glassy state, which is independent of temperature (*33*).

As discussed, the thermal effect on the structural properties of dried fish and fruits is less pronounced, thus yielding a partial glass transition in terms of temperature band and viscoelastic functions. Nevertheless, the fundamentals of a fully developed glass transition in amorphous polymers originate from the same dynamics of molecular chains as in curtailed vitrification due to partially ordered or crystalline matrices (*45, 46*). On the basis of this postulate, a potentially useful device can be conceived for the estimation of the extent of vitrification in partially glassy materials. This entails plotting of the first derivative of shear modulus as a function of sample temperature versus the sample temperature shown in **Figure 5** for the gelatin/cosolute mixture.

Gratifyingly, the storage modulus becomes the appropriate parameter for consideration, because its trace is reduced to a minimum at the conjunction of the WLF/free volume and Andrade theories. This reproduces the T_g value of −39.0 °C for the completion of the softening process in the ps4/cosolute mixture. On the basis of this principle, similar treatments were pursued for the viscoelastic behavior of partially amorphous tuna, abalone, apple, apricot, pear, plum, and date. As illustrated in **Figure 6**, these produced smooth first-derivative curves, with the relaxation spectrum of the viscous component of the network unraveling rapidly as compared to the solid element for all foodstuffs. The minimum of the storage modulus trace clearly demarcates the mechanical glass transition temperature for 70% tuna (−18 °C), 70% abalone (−22 °C), 67.2% apple (−43 °C), 67% apricot (−47 °C), 70.6% pear (−35 °C), 60.9% plum (−52 °C), 80.2% dates (−24 °C), and 83.8% dates (−20 °C) solids, respectively.

Concluding Remarks. The need to identify an objective way to assess the temperature dependence of molecular processes during vitrification led us to develop a glass transition temperature using small deformation dynamic oscillation. This is compared advantageously with early attempts to demarcate glassy phenomena, which produced empirical definitions of the mechanical T_g. Thus, dynamic mechanical thermal analysis (DMTA) in extension or bending mode attempted to identify the "right glass transition temperature" (*47, 48*). This has been taken as the initial drop in the values of storage modulus (E') upon heating or the maxima in loss modulus (E'') and tan δ traces within the realm of the rubber-to-glass transition. As has been pointed out by Peleg (*49*), however, in the absence of a distinct molecular process associated with these selections, the approach denotes merely an empirical index of convenience.

The prediction of the glass transition temperature obtained by treating the master curves in **Figure 4** with the WLF and Andrade equations unveils the passage from the glass transition region to the glassy state. Mechanistically, this coincides with the transformation from free-volume-derived effects in the glass transition to the process of an energetic barrier to rotation in the solid-like environment of the glassy state, thus assigning physical significance to the mechanical T_g. The approach can be extended to partially amorphous foodstuffs by identifying the function of storage modulus as the relevant indicator of molecular mobility during vitrification.

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