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Testing the validity of comparisons between the rheological and the calorimetric glass transition temperatures

Stefan Kasapis,[a,*] Insaf M. Al-Marhoobi,[a] John R. Mitchell[b]

[a]*Department of Food Science & Nutrition, College of Agricultural and Marine Sciences, Sultan Qaboos University, PO Box 34, Al-Khod 123, Oman*

[b]*Division of Food Sciences, University of Nottingham, Sutton Bonington Campus, Loughborough LE12 5RD, UK*

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Abstract

Dynamic mechanical techniques are used increasingly in the investigation of vitrification phenomena in biological materials, thus posing the question of whether the rheological T_g should be compared with the established practice of obtaining T_g values from differential scanning calorimetry. The nature of the rheological T_g is discussed and its frequency dependence is established with a view to facilitating comparisons with calorimetric data. Despite claims made in the literature, results on high sugar–κ-carrageenan mixtures, hydrated gelatin films, and thermoset epoxy resins demonstrate that there is no clear reference point for comparison of the glass transition temperatures derived with the two techniques. Furthermore, the structure-forming ability of κ-carrageenan and other biopolymers impacts primarily upon the mechanical manifestation of vitrification and contributes to the state of complexity of comparisons between thermal and mechanical data.

Keywords: Glass transition; κ-Carrageenan; Gelatin; Sugar; Rheology; Calorimetry

1. Introduction

For almost half a century, differential scanning calorimetry (DSC) has been used to measure as a function of temperature the difference in energy inputs into a substance and its reference, with both materials being subjected to a control temperature program.[1] Ten years ago, modulated DSC (MDSC) was commercialized in order to increase the sensitivity and resolution of thermal analysis, provide the heat capacity and heat flow in a single experiment, and measure the thermal conductivity.[2] As a result, complex transitions can be separated into molecular processes, with examples including the enthalpic relaxation that occurs at the glass transition region and the formation of metastable crystalline structures prior or during melting.[3] In synthetics and pharmaceuticals, calorimetry is used to determine the percentage of polymer crystallinity following processing (example, polyethylene terephthalate), the effect of plasticizer/water on vitrification temperature (examples, polyvinyl chloride, nylon), the feasibility of shipping solid petroleum pitch at elevated temperatures, the glass transition of amorphous drugs, etc. More recently, the technique has found a variety of applications in research of biological materials such as the glass transition of lactose, the sub-ambient transitions of frozen sucrose, and the isothermal crystallisation of concentrated starch systems, work which allowed the construction of the so-called 'state diagram'.[4,5]

Dynamic mechanical techniques were used extensively by Ferry and co-workers to study the vitrification properties of synthetic polymers and diluted systems.[6] Mechanical spectra of complex shear modulus or compliance obtained at fixed temperature intervals were overlaid horizontally along the log frequency (time) axis, using the time–temperature superposition principle, thus generating the four zones of viscoelastic behaviour.[7] The thermorheological simplicity achieved was rationalized in the glass transition region with the theory of free volume, which aimed to relate physical

* Corresponding author. Tel.: +968-515-256; fax: +968-513-418
E-mail address: stefan@squ.edu.om (S. Kasapis).

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parameters to molecular characteristics, see for example the classical results on a series of *n*-alkyl methacrylate polymers.[8]

Traditionally, researchers in biological macromolecules drew inspiration from 'the synthetic polymer approach', which was applied to the multifarious state transitions of biological glasses. These are complex mixtures of biopolymer/s, small polyhydric compounds, and water molecules thus requiring extreme caution when rationalizing their mechanical properties.[9] Nevertheless, softening dispersions were identified and glass transition temperatures (T_g) estimated using mainly dynamic mechanical thermal analysis (DMTA) in extension or bending mode and small deformation dynamic oscillation.[10,11] The present paper aims to discuss the grounds for pinpointing the rheological T_g in the viscoelastic spectrum in association with the summarily made comparisons with the calorimetric T_g.

In recent years, our efforts have focused on the structural properties of high sugar–biopolymer mixtures, which find increasing application in the food and pharmaceutical industries. Addition of κ-carrageenan at normal levels of industrial use (up to 1%) accelerates the mechanical manifestation of sugar vitrification, observed as a function of reducing temperature.[12] The present investigation takes advantage of this characteristic to examine the frequency dependence of the glass transition temperature.

2. Materials and methods

2.1. Samples

The sample of κ-carrageenan was a gift from Hercules, Lille Skensved, Denmark (batch X6960). ^{1}H NMR analysis showed that ι-carrageenan-like segments (that is with a sulphate group at position 2 of the 3,6-anhydride residue) constitute about 8% of the polymer. An Amberlite IR-120 exchanging resin from BDH was used to prepare the polysaccharide in the potassium form. κ-Carrageenan in the potassium form was characterized with intrinsic viscosity measurements [η] at a constant ionic strength (0.01 M KCl) and at 40 °C yielding a [η] value of 10.5 ± 0.2 dl g^{-1}.

2.2. Measurements

Measurements of the real (G'; storage modulus) and imaginary (G''; loss modulus) parts of the complex shear modulus ($G^* = G' + iG''$), and tan $\delta(G''/G')$ were performed with the Advanced Rheometrics Expansion System (ARES), which is a controlled strain rheometer (Rheometric Scientific, Piscataway, NJ, USA). The experimental temperature range was between 60 and −40 °C thus accessing molecular motions, which cover the glassy state, the softening dispersion (glass transition region) and the 'rubbery plateau'. Scan rate was 1 °C min^{-1}, the frequency of oscillation for each isochronal profile was between 0.1 and 100 rad s^{-1}, and the applied strain varied from 0.0008 in the glassy state to 1% in the rubbery plateau to accommodate the huge changes in the measured stiffness of the sample.

The polysaccharide was dissolved at 90 °C with stirring for 20 min and then the temperature was dropped to 70 °C for the addition of glucose syrup and KCl to the solution. Excess water was heated away to bring the total level of solids to the required concentration and then the sample was loaded onto the preheated parallel plate geometry of the rheometer (top plate diameter: 5 mm; measuring gap: 4 mm). The glucose syrup used was a product of Cerestar, Vilvoorde, Belgium. The dextrose equivalent of the sample was 42 and gel permeable chromatography provided the relationship between degree of polymerisation and surface area (%) of the spectrum of the material.[13] The total level of solids was 83% and glucose syrup compositions in this work refer to dry solids.

MDSC measurements were performed on a TA Instruments Calorimeter $Q1000$ with autosampler (TA Instruments Ltd, Leatherhead, UK). The instrument used a refrigerated cooling system to achieve temperatures of −90 °C and a nitrogen DSC cell purge at 25 mL min^{-1}. Hermetic aluminium pans were used. The DSC heat flow was calibrated using a traceable indium standard ($\Delta H_f = 28.3$ J g^{-1}) and the heat capacity response using a sapphire standard. Samples were rapidly cooled at an average of 20 °C min^{-1} to −90 °C, left there for 20 min, and the glass transition was determined from the midpoint of the heat capacity change observed at the heating rate of 1 °C min^{-1}. Samples of 7–10 mg were analysed at ± 0.53 °C temperature amplitude of modulation and 40 s period of modulation. The reference was an empty hermetically sealed aluminium DSC pan. Three runs were generally taken for both calorimetry and rheology and the average of essentially overlapping traces was considered as the glass transition temperature. Literature data on hydrated gelatin films were also considered to develop the discussion on meaningful comparisons of the vitrification phenomena of the two techniques.

3. Results and discussion

3.1. Frequency dependence of the mechanical rubber-to-glass transition

Vitrification is a kinetically determined process, which means that the mechanical manifestation of the rubber-to-glass transition will depend upon the period of observation. Thus increasing the frequency or decreasing

the time of measurement should result in spectacular changes in the viscoelastic functions obtained by an oscillatory experiment. This hypothesis is tested in the present communication using small deformation dynamic oscillation on a high sugar polysaccharide mixture made of 1% κ-carrageenan with added 30 mM KCl and in the presence of 81% glucose syrup.

Fig. 1 shows four graphs representing the dependence of shear moduli (G' and G'') and their tan δ ratio on temperature at constant frequency. It appears that the high sugar environment promotes a structural transformation, which exhibits very different thermal profiles of viscoelasticity than those of the aqueous gels. Instead of the well known solution-to-gel transformation induced by a drop in temperature,[14] the linear viscoelasticity of the high solid samples reproduces the master curve of amorphous synthetic polymers.[6,7] This result argues for the formation of lightly cross-linked junction zones, which interconnect amorphous chain segments thus imparting elastic properties to the polysaccharide network, as compared to brittle (aggregated) aqueous gels.

A substantial part of the master curve is unveiled, for example, in Fig. 1(b). Cooling and heating routines produce overlapping traces, which demarcate part of

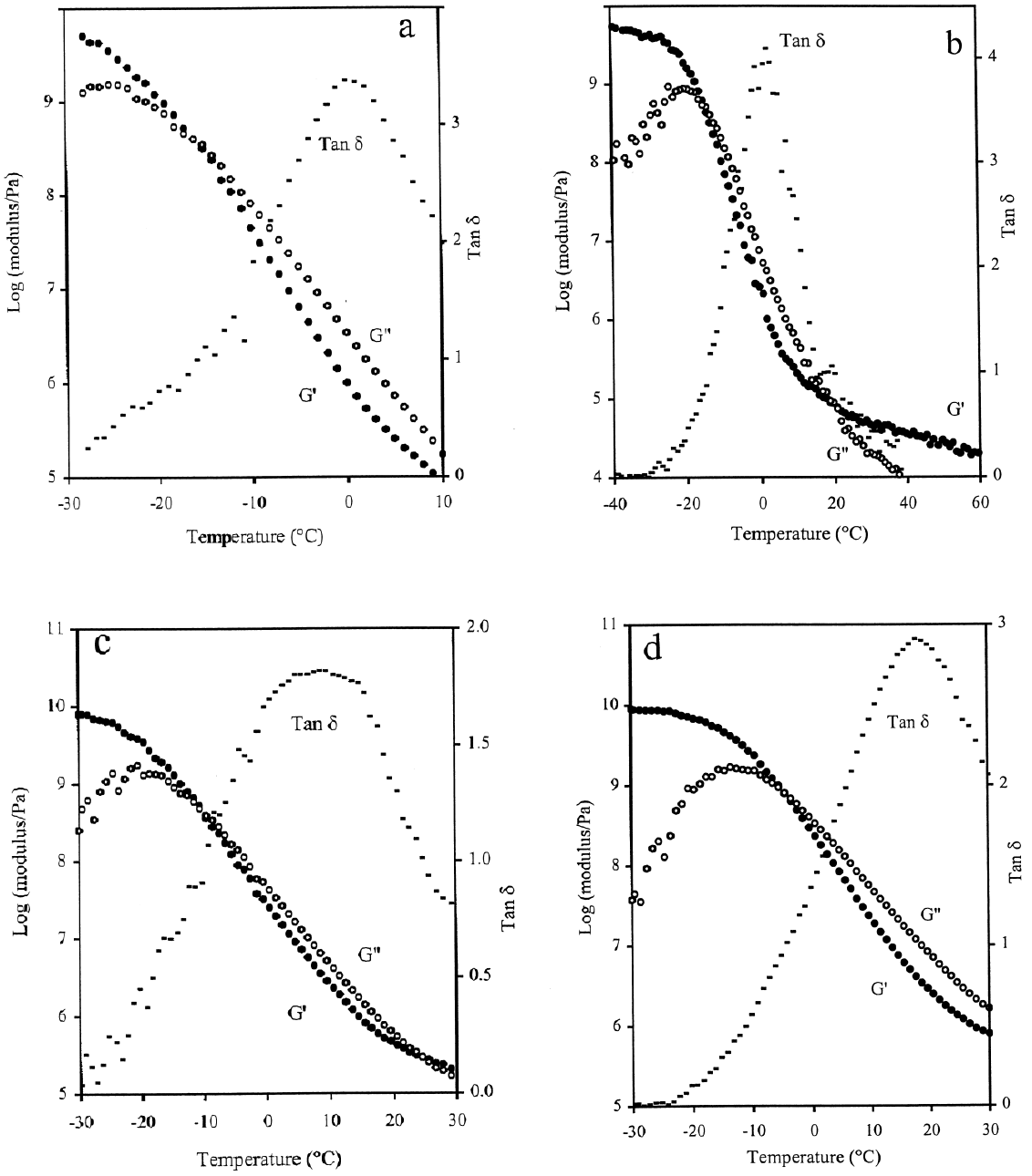

Fig. 1. Temperature variation of G', G'' and tan δ for 1% κ-carrageenan (30 mM KCl) plus 81% glucose syrup at: (a) 0.1; (b) 1; (c) 10; and (d) 100 rad s^{-1} (scan rate: 1 °C min^{-1}; strain from 0.0008 to 1%).

the rubbery plateau ($G' > G''$ from 60 to 20 °C), the softening dispersion or glass transition region ($G'' > G'$ from 20 to −15 °C) and the glassy state within the temperature range of −15 to −40 °C ($G' > G''$). At each frequency of oscillation (Fig. 1(a–d)), the passage from the softening region to the glassy state and the maximum in the G''/G' ratio are clearly discernible, thus begging the question of definition of the rheological glass transition temperature.

3.2. Empirical definitions of the rheological glass transition temperature

The need to identify an objective way to assess the temperature dependence of molecular processes during vitrification led to the comparison of the glass transition temperatures measured by whichever technique considered (mechanical, thermal, dielectric, NMR, etc.). Early attempts to determine the rheological glass transition temperature (T_{gr}) in biological materials followed the example of Angel who quoted values of steady shear viscosity (η) of 10^{12} Pa s for small-molecule inorganic liquids in the glassy state.[15] Difficulties are encountered due to the 'non-Newtonian' behaviour of the complex dynamic viscosity (η^*) of biopolymers, which for gelatin–sugar preparations in the glassy state descends steeply from 10^{11} to 10^8 Pa s with increasing frequency of oscillation from 0.1 to 100 rad s^{-1}.[16] Furthermore, it is rather difficult to experiment at conditions of extremely high viscosity evidenced in preparations of maltose and water. Readings did not exceed $10^{6.5}$ Pa s and a long extrapolation to 10^{12} Pa s was implemented using a modified form of the Arrhenius equation.[17,18] Large uncertainty necessarily accompanies such long extrapolations and the results or conclusions reached regarding the T_{gr} should not be taken seriously.

The mechanism of temperature-induced structural changes may be probed using DMTA but practical considerations limit the scope to obtain additional insights. To start with, the technique is better suited to the characterisation of solid materials moulded into rectangular bars and clamped tightly together by means of a screw. However, it is advantageous to use a measuring geometry (e.g., parallel plate) that can accommodate loading of hot melts thus being able to follow changes in viscoelasticity 'the whole distance' to the glassy state. DMTA heating runs are usually recorded from −80 to 120 °C but since it is difficult to seal hermetically the sample-clamp device, water loss affects the reliability of results at the high temperature end and diminishes the value of a subsequent cooling run.

Furthermore, sample bars, which are formed by pressing powders at about 10^8 Pa, are brittle and liable to develop localized stress effects, an outcome which increases the noise-to-signal ratio in the thermal profile of viscoelasticity. This issue is pertinent to the application of the time–temperature superposition principle at which overlaying of smooth mechanical spectra is required to signal the possible breakdown of thermorheological simplicity. Reverting to the heating profiles, the DMTA softening dispersions are unusually low in magnitude, namely between one and two decades of the Young's modulus, with the values of $\tan\delta$ remaining well below that of one (i.e., $E'' < E'$).[19]

As discussed in Section 3.1, both counts are in glaring contradiction to the archetype rubber-to-glass transition of amorphous synthetic polymers and should be attributed to reduced molecular mobility in the press-formed samples. In accordance to the synthetic polymer work, κ-carrageenan–glucose syrup mixtures produce glass transition regions of three to four orders of magnitude (G'' from about 10^5 to 10^9 Pa) and $\tan\delta$ maxima between 2 and 4 in Fig. 1. There is also some confusion in the literature as to what is the right glass transition temperature, which has been taken as the initial drop in the values of storage modulus (E') upon heating or the maxima in loss modulus (E'') and $\tan\delta$ traces.[20–22] However, in the absence of a distinct molecular process associated with these points, the approach denotes merely an empirical index of convenience.

3.3. Frequency dependence of a fundamental definition of the rheological glass transition temperature

In our view, Fig. 1 can be utilized to derive an index of physical significance that can be associated with the rheological glass transition temperature. The fundamental approach is based on the application of the time–temperature superposition principle and the concept of thermorheological simplicity pioneered by Williams, Landel, and Ferry (WLF) in amorphous synthetics.[6–8] For several biopolymer–sugar mixtures, including the κ-carrageenan–glucose syrup, it was demonstrated that the combined WLF/free volume framework holds in the softening dispersion.[23] In the glassy state, the temperature dependence of relaxation/retardation processes was better described by the predictions of the reaction rate theory. This outcome assigns physical significance to the glass transition temperature as the threshold of two distinct molecular processes, i.e., free volume effects which are superseded in the glassy state by a constant energy of activation required for local segmental motions. Based on this definition, the cross over of G' and G'' traces at the conjunction of the softening dispersion and the glassy state yields a T_{gr} of −15 °C in Fig. 1(b).

The definition of the fundamental T_{gr} has been advanced in detail earlier[23] but, for the first time, its frequency dependence is developed presently for comparisons with the calorimetrically derived glass transi-

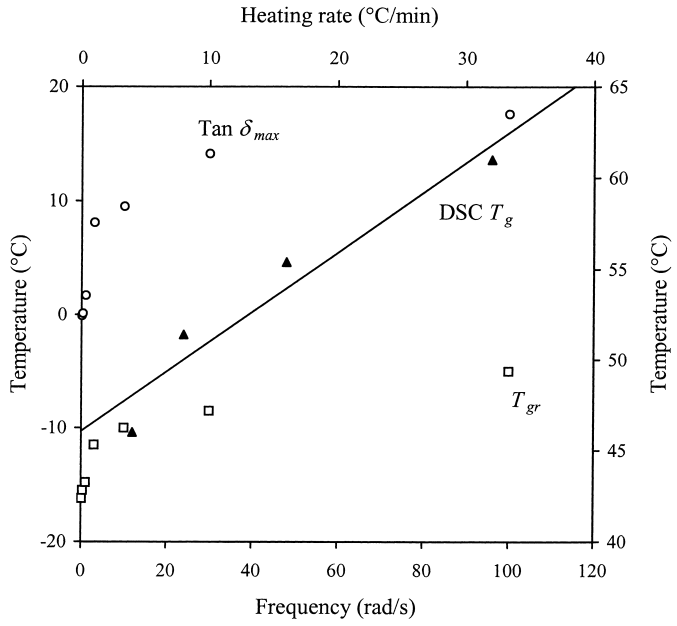

Fig. 2. The effect of frequency of oscillation on T_{gr} (□) and tan δ_{max} (○) of the sugar–κ-carrageenan sample in Fig. 1 (left y axis), and the effect of heating rate on the DSC T_g for gelatin films (▲) hydrated at 65% relative humidity (right y axis; points and linear fit from the original Ref. 29, with permission).

tion temperature. In doing so, data for all experimental frequencies, including the variation in the empirical tan δ peak are reproduced in Fig. 2.

Part of the work of Ferry and Fitzgerald was also carried out at a fixed scan rate (°C) thus producing 'isochrones' for poly(vinylchloride) gels (PVC) at a few selected frequencies.[6,24] In a complementary experiment, it was found that PVC complies with the principle of time–temperature superposition, which requires overlaying along the log frequency axis a series of 'isotherms or mechanical spectra' covering a wide range of experimental frequency (e.g., 0.1–100 rad s^{-1}). The set of shift factors (a_T) thus generated has a non-linear temperature dependence, which explains the lack of superposition of the corresponding isochrones by horizontal shifts along the temperature axis. For a given value of log shear modulus, the isochrone is sharper at low frequencies because it is occurring in a region of lower temperature where the factor a_T is changing more rapidly, as compared to high frequency temperature dispersions.

Similarly, the κ-carrageenan–sugar isochrones obtained at seven values of the oscillatory frequency are displaced on the temperature domain, as summarized for T_{gr} and tan δ_{max} in Fig. 2. Within the experimental frequency range (from 0.1 to 100 rad s^{-1}), T_{gr} increases 11° and, on average, the tan δ peak appears 20° higher in the thermal profile of viscoelasticity.

In a recent application of the coupling theory to synthetic macromolecules, Ngai and Plazek argue that the glass transition temperature can be considered as the temperature at which the relaxation time (τ) of the local segmental motions attains an arbitrary predetermined long time of, say, 100 s.[25] Based on this definition of T_g and the cooperativity between segmental motions of neighbouring molecules, a similar temperature dependence of vitrification properties was achieved for several polymers.[26] Satisfaction of the condition $\tau(T_g) = 100$ s signifies the rejection of tan δ as a valid marker of the glass transition temperatures and relates to our operational frequency of 0.1 rad s^{-1} for pinpointing the T_{gr}; lowest experimental frequency in Fig. 2.

It is anticipated that much attention will be focused in the area of cooperativity,[27] but its current framework of application to synthetic polymers creates a mathematical expression that resembles the WLF equation. The latter in conjunction with the concept of 'iso-free-volume' has been used to normalize the temperature dependence of viscoelasticity of biological glasses, and results were congruent with the aforementioned cooperativity work on synthetic systems.[23]

3.4. The calorimetric glass transition temperature

Ngai and Plazek hold the view that a T_g determined by the temperature dependence of the most probable relaxation or retardation times of the local segmental motions is more reliable than the values obtained from calorimetric measurements.[25] It is true that there is no clear-cut relationship between molecular mobility and thermal event in calorimetric experiments which forces researchers to resort to limiting factors in the form of T_{g1}, T_{g2} and T_{g3} for the onset, middle and completion of a particular case. MDSC thermograms obtained in this study for 82% glucose syrup, and 1% κ-carrageenan (30 mM KCl) plus 81% glucose syrup argue that there is very little change in the pattern of heat capacity in the presence of the polysaccharide. On average, the values of T_{g1}, T_{g2} and T_{g3} are -40.3, -30.1 and -18.9 °C, respectively (Fig. 3).

Nevertheless, glass formation is in the nature of a second-order thermodynamic transition, which is accompanied by a heat capacity change.[28] This is readily detectable for both model systems (Fig. 3) and commercial products (e.g., confectioneries) using DSC. Normal DSC involves a constant scan rate, which imposes no frequency effects on the collected data. Normally, those effects are of no concern in MDSC provided the modulation period, which determines frequency, is constant when comparing materials. Even in the situation where the period varies, frequency effects are insignificant because of the narrow range of useable periods of modulation (30–60 s).[3]

However, calorimetrically determined glass transition temperatures are affected by the heating rate, which should be reported. This is demonstrated in Fig. 2, alongside the rheology data, for mid-point glass transition temperatures of gelatin films. The films were hydrated at 65% relative humidity and analysed using DSC at the heating rates of 4 to 32 °C min^{-1}.[29] The gelatin data have been introduced in this context because they have been used in the last decade or so to advance a popular misconception on the comparison between the mechanical and thermal glass transitions temperatures, an issue which we are going to address next.

3.5. Two different techniques—one glass transition temperature?

A linear fit of the DSC glass transition temperatures of gelatin as a function of heating rate was attempted as illustrated in Fig. 2 and it was stated incorrectly that 'the zero heating rate T_g was approx 46.5 °C'.[29] However, it is clear from Fig. 2 that experimentation at lower heating rates would have followed an exponential T_g trend seen for the T_{gr} and tan δ_{max} values of κ-carrageenan–sugar mixtures at the low range of circular frequencies.

It was further argued, and it is today a popular belief among some practitioners in the field, that in synthetic polymers the rubber-to-glass transition obtained by dynamic mechanical techniques at 0.001 Hz corresponds to the DSC zero heating-rate T_g.[29] We were unable to find in the literature real evidence in support of this claim. Instead, Fig. 4 reproduces the isothermal cure of an epoxy resin monitored with MDSC and dynamic mechanical analysis (DMA) at 1 Hz.[30] The exothermic peak of curing, i.e., linear polymerisation followed by cross-linking of the epoxy coincides with a decrease in heat capacity due to reduction in diffusion mobility and free volume in the system. Evaluation by DMA demonstrates that the heat capacity changes at exactly the same time with the increase in Young's modulus measured at 1 Hz, an outcome that invalidates the preceding hypothesis. Failure to recognize this feature has led to some erroneous conclusions about the applicability of comparison between thermal and mechanical vitrification phenomena.

In order to make meaningful allowances for the measuring principles used in each technique, the dependence of T_{gr} and tan δ_{max} on frequency, and DSC T_g on heating rate have been plotted semi-logarithmically in Fig. 5. It should be remarked that the gradients of linear-log fits of mechanical and thermal events show the on-going effect of the experimental parameters, a result which makes non-kinetic determinations of T_g no longer appropriate. Vitrification phenomena can be further manipulated by annealing at a temperature above T_g shown for DSC thermograms of fructose solutions with a level of solids between 60 and 77%.[31]

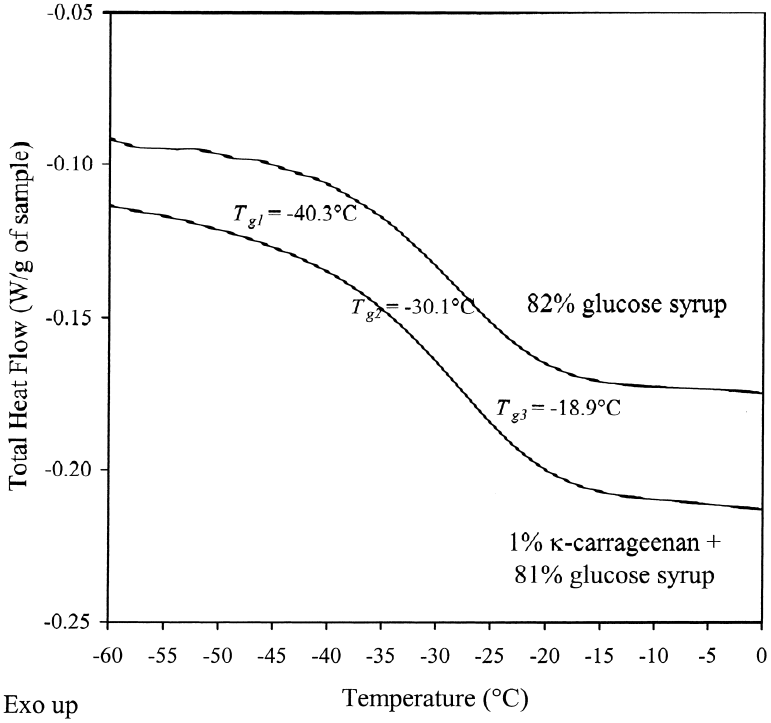

Fig. 3. Heat flow variation as a function of temperature for 1% κ-carrageenan (30 mM KCl) plus 81% glucose syrup and 82% glucose syrup obtained with MDSC at a heating rate of 1 °C min^{-1}.

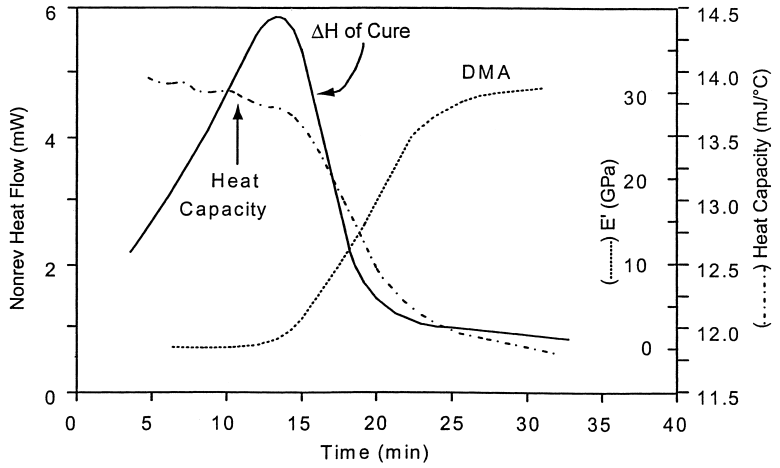

Fig. 4. Isothermal cure at 80 °C of an epoxy thermoset showing changes in heat capacity and non-reversing heat flow obtained at ±0.5 °C amplitude and 60 s period of modulation, and in storage Young's modulus recorded with DMA at frequency of 1 Hz (from Ref. 30, with permission).

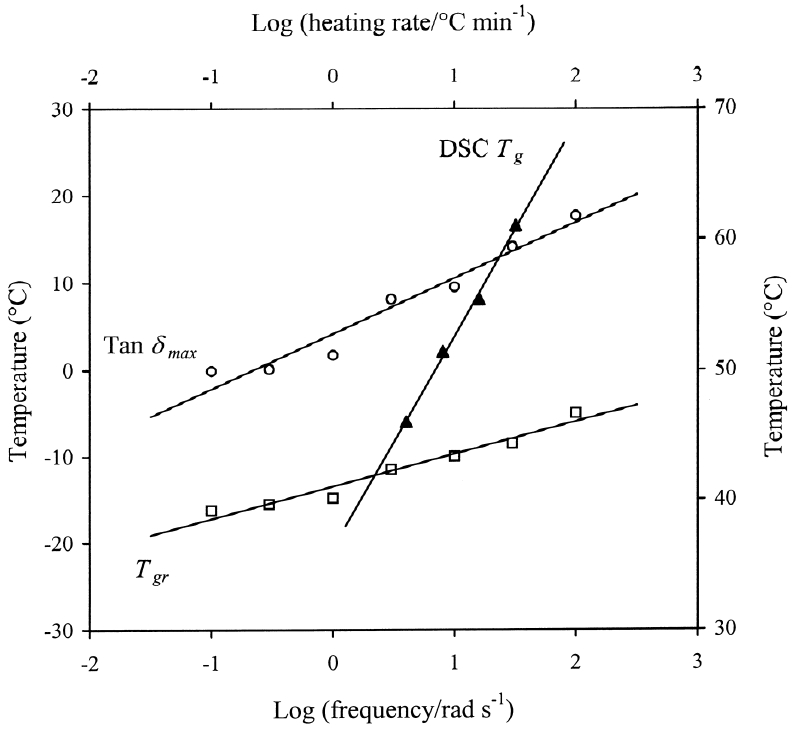

Fig. 5. Semi-logarithmic effects of frequency on T_{gr} and tan δ_{max} for the sugar–κ-carrageenan sample in Fig. 1 (left y axis), and of heating rate on the DSC T_g for gelatin films in Fig. 2 (right y axis).

As a final demonstration of the care that must be taken in interpreting rheological and calorimetric data, we compare the T_g values of κ-carrageenan–sugar systems obtained at the same level of solids using both techniques. Figs. 2 and 5 show that the glass transition temperature (T_{gr}) of 1% κ-carrageenan (30 mM KCl) plus 81% glucose syrup at the lowest experimental frequency of oscillation (0.1 rad s^{-1}) is about −16 °C. Comparative MDSC readings of our mixture or a single preparation of 82% glucose syrup produces mid-point glass transition temperatures of about −30.1 °C (Fig. 3). Similar work on several mixtures of sugar with polysaccharide or gelatin unveiled a temperature differential of up to 25° between T_{gr} and DSC T_g.[32]

Results suggest that unlike the DSC T_g, the rheological T_g is affected by the nature of the biopolymer and cannot be predicted by the basic mathematical expressions for mixed systems such as the Couchman–Karasz equation.[33] It does appear that the apparent increase in the T_{gr} is related to the ability of the biopolymer to

form a network,[13,14,23] a process which rheology is extremely well qualified to follow. In contrast, calorimetry provides information primarily on the mobility of the sugar phase and the small addition of biopolymer is a mere cross-contamination.

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