



Combined use of the free volume and coupling theories in the glass transition of polysaccharide/co-solute systems

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ABSTRACT

The structural properties of the glass dispersion in agarose, κ -carrageenan and deacylated gellan with co-solute (glucose syrup) at 80.0% (w/w) solids were studied. Investigative techniques were small-deformation stress relaxation and dynamic oscillation on shear. Vittrification was monitored between -2 and -50 °C with continuous thermal runs and isothermal frequency or time sweeps obtained at constant temperature intervals. The time–temperature superposition principle was utilized to compose master curves. The Williams, Landel and Ferry equation was able to pinpoint the network T_g for these systems as the turning point from the predictions of the free volume theory in the transition region to those of the reaction rate theory at the glassy state. Further insights into the physics of intermolecular interactions at the vicinity of T_g were obtained using the coupling model of molecular dynamics in the form of the Kohlrausch, Williams and Watts function. The model described well the spectral shape of the local segmental motions in polysaccharide/co-solute samples at the short-time region of the stress–relaxation master curve. Analysis provided the intermolecular interaction constant and apparent relaxation time, which are valuable parameters for the elucidation of structural morphology at T_g .

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1. Introduction

In the last 80 years or so that the scientific understanding of glassy systems has evolved, a fundamental question was the thermodynamic or kinetic nature of vitrification (Parks & Huffman, 1926). Glasses are formed when a liquid or a rubbery system is cooled so rapidly that there is no time for the molecules to rearrange themselves and pack into crystalline domains (Hutchinson, 1995). At the ‘glass transition region’ there is a continuity in the primary thermodynamical variables of volume, enthalpy and free energy. On the other hand, the first derivative variables of coefficient of expansion (α_p), heat capacity (C_p), etc. undergo marked changes in the course of a very few degrees (Allen, Blanshard, & Lillford, 1993). Furthermore, the spike in α_p and C_p observed at the crystallization temperature has no counterpart during vitrification. The process is considered to be in the nature of a second order thermodynamic transition in which the material undergoes a change in state but not in phase. In this context, an important consideration is the concept of plasticization and its effect on the glass transition temperature, T_g (Momany & Willett, 2002). A plasticizer is defined

as a low molecular-weight substance incorporated in a material to increase its workability, flexibility or extensibility (Perry & Donald, 2002).

There is as yet no fully satisfactory theory of glass transitions but there are several valuable ways of describing them in a quantitative fashion (Montserrat, Roman, & Colomer, 2003). Synthetic science, in particular, the subject of the viscoelasticity of polymers has reached a notable level of development (Nandan, Kandpal, & Mathur, 2003), and it would make “a world of difference” if the sophisticated synthetic polymer approach could be extended to the structural conundrums of biomaterials. A certain approach used by polymer scientists to develop a mechanistic understanding of the rubber-to-glass transition is based on the concept of molecular free volume (Ferry, 1991). According to this, holes between the packing irregularities of long chain segments or the space required for their string-like movements account for free volume. Adding to that the space occupied by the van der Waals radii of polymeric contours and the thermal vibrations of individual residues, i.e. the occupied volume, we come up with the total volume per unit mass of a macromolecule. In polymer melts the proportion of free volume is usually 30% of the total volume, and the theory predicts that it collapses to about 3% at the glass transition (Cangialosi, Schut, van Veen, & Picken, 2003).

Recently, the “coupling model” has been put forward to refine analysis based on the premise that intermolecular interactions are

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more fundamental than free volume and that they are the ultimate determining factor of molecular dynamics in densely packed polymers (Ngai, 2000a). It was also felt that in order to follow structural properties within the broad glass transition region, the theory of free volume might have been unable to pinpoint the precise molecular dynamics operating at T_g (Alves, Mano, Gomez Ribelles, & Gomez Tejedor, 2004). The coupling model allows the development of a connection between the conformational chemistry of monomers and the glassy behavior of polymer, with strongly interacting systems exhibiting high values of the coupling constant, n , and an apparently broad distribution of relaxation times (Robertson & Rademacher, 2004). The parameter n need not be constant during a relaxation, hence the approach is not thermorheologically simple (TS), which is a basic assumption of the free volume theory (Robertson & Palade, 2006).

Work on polymer–solvent mixtures, polymer blends and block copolymers will provide additional tests as to the general applicability of the aforementioned framework of thought. In biomaterials, a start has been made by examining the relaxation dynamics of gelatin/co-solute mixtures throughout the glass transition region and at the vicinity of T_g (Kasapis, 2006). The present communication deals with the vitrification of polysaccharide/co-solute mixtures in conjunction with the published literature on gelatin and amorphous synthetic polymers.

2. Materials and methods

2.1. Materials

Polysaccharides agarose, κ -carrageenan, and deacylated gellan were selected for the current study due to their common gelling mechanism of coil-helix transition. Agarose (Type 1-B) was purchased from Sigma–Aldrich, Gillingham, UK. It is a material of high gel strength recorded for 2.0% (w/w) polymer concentration in aqueous preparations of a previous investigation ($G' \sim 34$ kPa at 0 °C) (Shrinivas, Kasapis, & Tongdang, 2009). Using aqueous size exclusion chromatography, the supplier determined the number average molecular weight of this agarose sample ($M_n \sim 120$ kDa). Furthermore, moisture, ash and sulfate contents were of less than 10%, 0.25% and 0.12%, respectively (w/w).

The sample of κ -carrageenan was a gift from Hercules, Lille Skensved, Denmark. ^1H NMR analysis showed that ι -carrageenan-like segments (i.e. with a sulfate 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, $[\eta]$, at constant ionic strength (0.01 M KCl) and 40 °C yielding $[\eta] = 10.5 \pm 0.2$ dl/g (Kasapis & Al-Marhoobi, 2005).

The deacylated gellan sample used in this investigation was a gift from NutraSweet Kelco Company, Tadworth, UK, and it came in the sodium form. Finally, the glucose syrup used presently was a gift from Cerestar (Mechelen, Belgium). It is prepared by controlled α -(1-4)-amylase hydrolysis of wheat starch, with about 82% (w/w) amylopectin content, down to glucose sequences linked by α -(1 \rightarrow 4) and α -(1 \rightarrow 6) glycosidic linkages. The dextrose equivalent (DE) of the material is 42, the level of solids is 83.0% (w/w), and the water content of glucose syrup was taken into account in the calculation of the total level of solids for sample preparation.

2.2. Methods

To prepare high-solid samples, polysaccharides were dissolved in deionized water at 90 °C with stirring for 15 min and then the temperature was dropped to 70 °C for the addition of glucose syrup.

A solution of calcium chloride was introduced into the sample of deacylated gellan at 70 °C to obtain 7.5 mM Ca^{2+} in the final mixture. In the case of κ -carrageenan, a solution of potassium chloride was used to obtain 10 mM K^+ in the final mixture. Excess water was evaporated off to bring the total level of solids to 80.0% (w/w). The polysaccharide content in final formulations ranged between 0.5% and 2.0% (w/w). All sample compositions mentioned below will be on w/w basis. Samples were loaded onto the preheated platen of the rheometer at 60 °C for subsequent experimentation. Throughout the temperature ramp (60 to -50 °C) they remained clear to the naked eye and adhered readily to the driving surface of the instrument. In general, the experimental temperature range was wide enough to observe a transformation from the melt to the glassy state in preparations (see, for example, Fig. 1).

Small-deformation dynamic oscillation and stress relaxation experiments on shear were used to provide readings of the storage modulus (G') which is the elastic component of the network, loss modulus (G'' ; viscous component), dynamic viscosity (η^*), and stress relaxation modulus, $G(t)$. Variations with time and temperature were further assessed as a measure of the 'damping factor' ($\tan \delta = G''/G'$) of the relative liquid-like and solid-like structure of the material (Malkin & Isayev, 2006). Measurements were performed with the Advanced Rheometrics Expansion System (ARES), which is a controlled strain rheometer (TA Instruments, New Castle, DE). ARES has an air-lubricated and essentially non-compliant force rebalance transducer with the torque range being between 0.02 and 2000 g cm. Parallel-plate geometry of 5 mm diameter was used and gap was kept at 1 mm.

The exposed edges of samples within the parallel-plate measuring geometry were covered with a silicone fluid from BDH (50 cS) to minimize water loss. Samples were then subjected to a controlled cooling run (scan rate: 1 °C/min) at the frequency of 1 rad/s, hence obtaining dynamic oscillatory data. Isothermal time dependence of mechanical relaxation was assessed by transient stress relaxation tests throughout the range of -50 to -2 °C at temperature intervals of 3 °C. Samples were allowed to equilibrate isothermally for 10 min following application of an instantaneous strain. This was varied from 0.02% to 1% in order to accommodate the huge changes in the measured stiffness of the sample as a function of temperature.

Three replicates were analyzed for each experimental preparation, with the rubber-to-glass transition being readily reproducible within a 3% error margin as a function of temperature or timescale of measurement. The nonlinear regression was carried out using GraphPad Prism Version 4.03.

3. Results and discussion

3.1. Dynamic oscillatory measurements as a means of observing molecular relaxations in polysaccharide/co-solute systems

The present work constitutes a demonstration of the applicability of the synthetic polymer approach to the multifarious state transitions of high-solid biomaterials. The melt-to-glass transformation of polysaccharides (or gelatin) in the presence of co-solute is of fundamental and technological interest since these systems find widespread applications in processed foods and as excipients in pharmaceuticals (Afoakwa, Paterson, & Fowler, 2007; Rahman, 2006). An expedient protocol to obtain information on the structural properties of these materials is to examine the variation in G' and G'' traces as a function of temperature at a constant frequency or time of observation. This is illustrated in Fig. 1(a–c) for typical preparations of agarose, κ -carrageenan and deacylated gellan in the presence of glucose syrup as the co-solute, with the total level of solids in each case being adjusted to 80.0%.

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