

Enthalpy and mechanical relaxation of glassy gelatin films

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Abstract

The structural relaxation during the ageing of glassy gelatin films containing 8, 12 and 17% water at 25 °C was studied through (i) the extent of relaxation enthalpy (ΔH) associated with physical ageing using Differential Scanning Calorimetry (DSC) and (ii) the changes in storage modulus (E') measured isothermally in the bending mode at different frequencies using Dynamic Mechanical Thermal Analysis (DMTA). The E' increased with increasing ageing time (t_a) and measurement frequency. For a given water content, the rates of ageing extracted through time-ageing time superposition of E' data was in agreement with the rate of increase of ΔH . The rate and extent of ageing increased with the water content.

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1. Introduction

When liquid materials are quenched to temperatures below their glass transition temperature (T_g), their structures are immobilised in the glassy, non-equilibrium state. ‘Quenching’ in the context of biopolymers can be achieved through rapid cooling or rapid drying, i.e. removal of the plasticising water. Glassy materials are ‘kinetic solids’, which are thermodynamically unstable and thus are subjected to time-dependent changes. These changes are known as physical ageing, the basic feature of glassy materials being polymeric, organic, or inorganic (Struik, 1978). During the ageing process, physical properties such as enthalpy and volume decrease and these changes are accompanied by important changes in transport properties and more relevant to this study, changes in mechanical properties such as modulus, compliance and mechanical relaxation time (Spinu & McKenna, 1997; Struik, 1978).

While most of the studies of physical ageing of biopolymers focus on measuring the enthalpy relaxation process using DSC (Chung & Lim, 2004; Cowie, Ferguson, Harris, & McEwen, 1998a; Kim, Suzuki, Hagiwara, Yamaji, & Takai, 2001; Livings, Breach, Donald, & Smith, 1997; Lourdin, Colonna, Brownsey, Noel, & Ring 2002; Thiews & Steeneken, 1997), some studies also report the changes in mechanical properties of biopolymers in the glassy state. Shogren and Jasberg (1994)

measured the tensile strength of high-amylose starch extrudates during ageing and correlated the increase of tensile strength to the enthalpy relaxation measured using DSC. Recently, Lourdin et al. (2002) used three-point bend test to study the mechanical relaxation behaviour of maltose–water and starch–sorbitol–water systems as a function of ageing time. These authors found qualitative correlations between the enthalpy relaxation measured by DSC and the changes to mechanical relaxation times and volume change measured by dilatometry.

Gelatin is a water-soluble protein obtained from collagen by acid or alkaline hydrolysis (Ward & Courts, 1977). Some of its most important applications (pharmaceutical capsules, photographic films, etc.) result from its ability to form flexible glassy films. Very often, at low water content, gelatin exists as a partially crystalline glassy polymer depending on the processing thermal history (Swan & Torley, 1991). Physical ageing and its impact on mechanical properties of gelatin films stored below their T_g are therefore of significant technological importance.

The aim of this study was to investigate changes in the mechanical properties of partially crystalline gelatin films in the glassy state and relate these changes to the more readily measurable and hence more widely used approach of determining enthalpy relaxation using DSC.

2. Materials and methods

Gelatin was purchased from Sigma (225 bloom, type B from bovine skin) and contained 11% water content (w.b.) as determined by oven drying (105 °C, overnight). The gelatin powder (~30 g) was hydrated by adding water (in small droplets) and mixing using a laboratory rotary mixer (~10 min) and then

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used to produce films (thickness of ~ 0.7 mm) by pressing the pre-hydrated powder ($23 \pm 0.3\%$ water, wet basis) using a heated hydraulic press (pressure, 2.5×10^7 Pa; temperature, 100°C ; time, 5 min), i.e. above the glass transition temperature of amorphous fraction. The films, which were formed between two standard photocopy grade office transparencies, were cooled rapidly to room temperature (below T_g) by placing them over a cold surface (set to a nominal temperature of -10°C). A range of water contents was achieved by subsequently equilibrating the films at room temperature for 4 weeks over different salt solutions providing a range of relative humidities (RH). The salts used were LiCl (RH $\approx 11\%$), MgCl_2 (RH $\approx 33\%$), and CuCl_2 (RH $\approx 68\%$) (Nyqvist, 1983) leading to water contents of 8 ± 0.2 , 12 ± 0.7 and $17 \pm 0.3\%$ (wet basis, w.b.).

2.1. DSC analysis

Approximately 40 mg sub-sample of gelatin film was packed and sealed in a pre-weighed high pressure stainless steel pan. The glass transition (T_g) and melting (T_m) temperatures were determined by heating using a Perkin Elmer Pyris Diamond DSC calibrated for temperature and enthalpy with Indium ($T_{m,\text{onset}} = 156.6^\circ\text{C}$, $\Delta H = 28.45$ J/g) and cyclohexane ($T_{m,\text{onset}} = 6.5^\circ\text{C}$). The reference was an empty stainless steel pan. After the first heating, the samples were cooled at a rate identical to the rate of heating ($10^\circ\text{C}/\text{min}$), and then the second heating cycle was performed. T_g was determined from the onset, midpoint and endpoint of the step-change in the specific heat of the sample in the second heating run while T_m was reported as onset, peak and endpoint temperatures obtained from the first heating scan (Fig. 1).

Sub- T_g thermal history was ‘eliminated’ by heating the sample to a temperature T_{max} , where $T_{g,\text{end}} < T_{\text{max}} < T_{m,\text{onset}}$. The samples were then cooled to 25°C (ageing temperature) at a cooling rate identical to the heating rate ($10^\circ\text{C}/\text{min}$); the pans were removed from the DSC and stored in an incubator set to $25 \pm 1^\circ\text{C}$. The samples (same pans) were analysed by DSC after different ageing times (0–72 h) as described above.

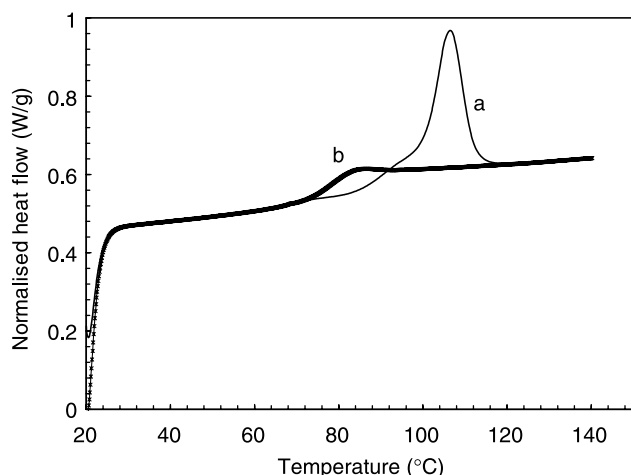


Fig. 1. First (a) and second (b) heating DSC thermograms of gelatin film containing 12% water content (w.b.).

2.2. DMTA analysis

The sub- T_g thermal history of the films (length ~ 20 mm, width ~ 9 mm, thickness ~ 0.7 mm) was eliminated in a similar way to that described above. The samples were in an oven heated set to $5\text{--}10^\circ\text{C}$ above $T_{g,\text{end}}$, i.e. still below $T_{m,\text{onset}}$ (as defined by DSC), while the samples were sealed using Araldite between two microscopy glass slides in order to minimise water loss. The samples were then cooled to the ageing temperature of 25°C , removed from between the glass slides, and coated with silicon oil to alleviate changes in water content during the ageing study.

The ‘fresh’ films were mounted in a Rheometric Scientific Dynamic Mechanical Thermal Analyser (DMTA IV) using the single-cantilever bending mode geometry. A constant strain of 0.03% and five different frequencies of 0.1, 0.2, 0.5, 1, 4 and 10 Hz were selected. The temperature was maintained constant at $25 \pm 0.1^\circ\text{C}$ during the experiment and the E' was determined over the ageing period of 0–72 h.

The results were then analysed using the concept of ‘time-ageing time’ superposition proposed by Struik (1978) for representing experimental data related to the effect of ageing on the small-strain creep properties. This is based on the proposition that the main rheological effect of ageing of glassy polymers is the increase in relaxation time. In this approach, the creep (and stress relaxation) curves obtained at different ageing times t_a after quenching to the ageing temperature can be shifted along the time axis and superimposed to form a single master curve (Robertson, Monat, & Wilkes, 1999; Spinu & McKenna, 1997). This assumes that the changes of all relaxation times probed are consistent and therefore the shape of the creep or stress relaxation (or modulus as is the case in this study) response does not change with the ageing time. The rate of ageing can then be characterised from the ratio of logarithm of the ageing time shift factor a_{t_a} versus t_a . The double logarithmic shift rate μ is then defined as:

$$\mu = \frac{d(\log a_{t_a})}{d(\log t_a)} \quad (1)$$

a_{t_a} is determined for each t_a relative to an arbitrary reference ageing time. The rate of ageing process could be characterised by μ .

3. Results and discussion

3.1. Phase behaviour

Typical DSC thermograms of gelatin film containing 12% water are shown in Fig. 1. During the first heating scan, two endothermic events were observed. First a step change in heat flow was assigned to a glass-to-rubber transition relating to the amorphous regions of biopolymer, which are in the glassy state at the water contents of interest at room temperature (Mousia, Farhat, Blachot, & Mitchell, 2000; Pinhas, Blanshard, Derbyshire, & Mitchell, 1996). The glass transition was followed by an endotherm associated with the melting and dissociation of

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