



Reduction of enthalpy relaxation in gelatine films by addition of polyols

Paulo Díaz-Calderón^a, Bill MacNaughtan^b, Sandra Hill^b, John Mitchell^b, Javier Enrione^{a,*}

^a Biopolymer Research and Engineering Laboratory (BIOPREL), School of Nutrition and Dietetics, Universidad de los Andes, Chile. Monseñor Alvaro del Portillo 12.455, Las Condes, Santiago, Chile

^b Division of Food Sciences, The University of Nottingham. Sutton Bonington Campus, Loughborough LE12 5RD, United Kingdom



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ABSTRACT

The aim of this study was to evaluate the effect of plasticisers with different molecular weights (glycerol and sorbitol) on the structural relaxation kinetics of bovine gelatine films stored under the glass transition temperature (T_g). Plasticisers were tested at weight fractions of 0.0, 0.06 and 0.10. Films conditioned in environments under $\sim 44\%$ relative humidity gave moisture contents (w/w) in the range 0.14–0.18. The enthalpy relaxation (ΔH) was determined using differential scanning calorimetry (DSC). Samples used had T_g values in the range 24–49 °C. After removing the thermal history (30 °C above T_g , 15 min), samples were isothermally stored at 10 °C below T_g for between 2 and 80 h. The addition of plasticisers induced a significant reduction in the rate of structural relaxation. The linearisation of ΔH by plotting against the logarithm of ageing time showed a reduction in the slope of samples plasticised with both polyols. The reduction in relaxation kinetics may be related to the ability of polyols to act as enhancers of molecular packing, as recently reported using positron spectroscopy (PALS). However, a direct correlation between the relaxation kinetics and the plasticiser's molecular weight could not be established, suggesting that this phenomenon may be governed by complex molecular gelatin-plasticiser-water interactions.

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1. Introduction

The structural stability of a polymeric material depends on the matrix's physical state (molecular arrangement), solid content (or humidity content) and temperature. Thus, a molecularly arranged solid, such as in the case of a crystal, will have different stability levels compared to amorphous or molecularly disorganised materials, which are characterised by the lack of a regular arrangement at the molecular level which implies that exact position of a molecule at a given time cannot be defined [1]. Amorphous structures are obtained in a series of processes in the food industry (e.g. baking, concentration, freeze drying, spray drying and extrusion), in which the moisture removal stage or temperature reduction (freezing) occurs in short time intervals [2,3]. During storage, a polymeric material tries to reach a condition of thermodynamic equilibrium based on the surrounding environment, and it does so by structural adjustments that are determined by the matrix's physical state and temperature. In the case of amor-

phous polymers stored below the glass transition temperature (T_g), the molecular mobility is strongly restricted due to the system's high viscosity ($\sim 10^{12}$ Pa s⁻¹) [4–6]. Under such conditions, the material tends to reach thermodynamic equilibrium through micro-structural changes associated with the release of energy (ΔH) and a decrease in the specific volume (densification) in a phenomenon known as structural relaxation or physical ageing [7,8]. Notably, this is a spontaneous phenomenon widely studied in synthetic polymers [9–15], but additional research is required in the biopolymer area due to the technological the material, for example, an increase in the elastic modulus [16–18] increase in fragility [19] and decrease in permeability and diffusion [20–23]. This behaviour may be governed by the structural modification associated with a more compact molecular arrangement and an increase in the degree of molecular interaction caused by the relaxation phenomenon [7].

The scientific literature has shown that the presence of low-molecular-weight compounds (plasticisers) in a polymeric matrix in the glassy state produces important structural changes, which, at a macroscopic scale, are associated with a decrease in the matrix's specific volume. This behaviour has been reported in amorphous matrices based on maltodextrin with different molecular weights

* Corresponding author.

E-mail address: jenrione@uandes.cl (J. Enrione).

Table 1
Moisture content and Tg in gelatine-glycerol and gelatine-sorbitol films*.

Glycerol Content (Qg)	Moisture Content (Qw)	Tg _{onset} (°C)
0.00	0.18 (0.00014)	49.1 (0.3)
0.06	0.16 (0.021)	33.8 (2.5)
0.10	0.14 (0.00030)	24.3 (2.1)
Sorbitol Content (Qs)	Moisture Content (Qw)	Tg _{onset} (°C)
0.00	0.18 (0.00014)	49.1 (0.3)
0.06	0.16 (0.055)	35.6 (0.4)
0.10	0.16 (0.013)	29.4 (1.4)

* Values between the parentheses correspond to the standard deviation.

[24], maltopolymer-maltose [25] and high dextrose equivalent (DE) maltodextrin and glycerol [26] using gas pycnometry. Diaz et al. [27] also described a similar behaviour in bovine gelatine films plasticised with different glycerol levels using the same technique. This behaviour is quite surprising because the classic material science literature states that the presence of plasticisers produces an increase in the molecular mobility of the system, a phenomenon that may be governed by an increase in the inter-molecular space (or free volume) and a decrease in viscosity at a local level [28–30]. This phenomenon should be associated with an increase in the system's specific volume, which would explain the fact that plasticisers are used in the industry to increase the flexibility and extensibility of polymeric materials, facilitating their management on the processing level [1]. However, studies at the nano-structural level carried out in biopolymers in the glassy state using positron annihilation lifetime spectroscopy (PALS) have reported that at the sub-nanometric scale, a plasticiser produces a decrease in the volume of free spaces (Vh) that exist between polymeric chains, generating an increase in the molecular packing of matrix [25,31,32]. In amorphous polymeric systems, these free spaces are generated due to an irregular molecular arrangement that is characteristic of structurally disorganised materials (amorphous). In this context, it has been proposed that the decrease in Vh may be due to the capacity of low-molecular-weight compounds to occupy these empty volumes of sub-nanometric dimensions [26]. This behaviour has been described in glassy amorphous matrices based on maltodextrins of different DEs [24,31], maltopolymer-maltose mixes [25] and maltodextrin (DE12)-glycerol [26]. Recent studies have reported the effect of molecular packing by the addition of glycerol and sorbitol in amorphous films based on bovine gelatine in the glassy state [33–35]. These nano-structural changes may help to explain the decrease in moisture sorption that is observed in glassy biomaterials in the presence of plasticisers [27,36–38]. Here, it has been proposed that as a polymeric matrix is denser and more compact, it is more difficult for a water molecule to interact with the matrix's sorption sites, which, under these conditions, would also be occupied by the plasticiser [26,37]. Additionally, a strong dependence of the Vh value as a function of temperature has been reported with a clear inflection point at a temperature equal to Tg; since a very good correlation has been found between Tg values

obtained using PALS and those calculated using differential scanning calorimetry (DSC) [26,33,35].

Therefore, the structural changes produced by the presence of low-molecular-weight compounds in a glassy polymeric matrix suggest that the presence of plasticisers could have a significant effect on the structural relaxation kinetics that occur below Tg. The aim of this study was to determine the effect of glycerol and sorbitol (commonly used plasticisers in the food and pharmaceutical industries) on the structural relaxation kinetics (physical ageing) of bovine gelatine films in the glassy state.

2. Methods

2.1. Sample preparation

The bovine gelatine films (Rousselot, Bloom 220, Brazil) were prepared using the cold casting technique (5 °C) and by adding glycerol (Merck, molecular weight 92.10 g/mol, Germany) and sorbitol (Blumos, molecular weight 182.17 g/mol, Chile) as plasticisers. Preparing the films at 5 °C would promote a stable structure by formation of triple helices associated to gelling. All samples were heated to remove the crystalline fraction in order to generate fully amorphous samples.

The plasticiser was added to a 7% (w/v) gelatine suspension in weight fractions (Q_x) of 0.0, 0.02, 0.06 and 0.10 (Q_x = plasticiser weight/(plasticiser weight + gelatine weight)). The suspensions were deposited on Teflon moulds and kept in an environment with ~0% relative humidity using P₂O₅ for at least a week. They were then conditioned under environments with constant relative humidity (44%, K₂CO₃ saturated solution) until reaching gravimetric equilibrium, that is, until the weight difference between two consecutive measurements was lower than 0.5%.

2.2. Glass transition temperature and enthalpy relaxation

The Tg value of each sample was determined using DSC (Pyris Diamond, Perkin Elmer, USA). The equipment was calibrated using Indium as a standard (T_m = 156.6 °C and ΔH = 28.4 J/g). Next, ~20 mg of each sample was hermetically sealed in stainless steel capsules of 60 μL, while an empty capsule was used as a reference. The methodology used was as follows: heating from –20 °C to 120 °C at 10 °C/min (complete melting of crystalline fraction in all samples), maintaining 120 °C for 2 min, cooling from 120 to –20 °C at 40 °C/min, maintaining –20 °C for 2 min and heating from –20 °C to 120 °C at 10 °C/min. The Tg was considered as the temperature value of the transition onset associated with the change in heat capacity (Cp) observed in the second temperature scan. All the samples were analysed in triplicate.

The enthalpy relaxation kinetics (physical ageing) were determined using DSC after the removal of the thermal history of the samples. For this process, the samples were kept at a constant temperature Te (Te = Tq_{endset} + 30 °C) for 15 min [39,40]. Then, the

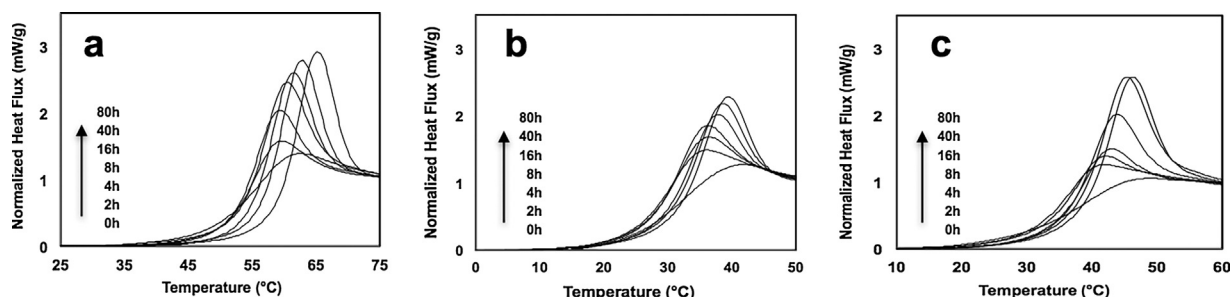


Fig. 1. Enthalpy relaxation in gelatine films (a) and those plasticised with glycerol 0.10 (b) and sorbitol 0.10 (c) at different ageing time (hours).

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