

# Water sorption and thermo-mechanical properties of water/sorbitol-plasticized composite biopolymer films: Caseinate–pullulan bilayers and blends

Eleana Kristo, Costas G. Biliaderis\*

Laboratory of Food Chemistry and Biochemistry, Department of Food Science and Technology, School of Agriculture, Aristotle University, GR-541 24, Thessaloniki, Greece

Received 21 July 2005; accepted 10 November 2005

## Abstract

The moisture sorption and thermo-mechanical behavior of pullulan, sodium caseinate and their blend and bilayer films (weight polymer ratio 1:1) were studied. All plain and composite films containing the same level of sorbitol showed very similar equilibrium water content. Incompatibility between both polymers was assumed, since separate  $\tan \delta$  peaks corresponding to those of the two pure components, were observed in the DMTA thermal traces of their blends containing 25% w/w (dry solids) sorbitol. The thermo-mechanical properties of polyol-free blends and bilayers were governed by pullulan, as their behavior was too similar to that of pullulan alone. The plasticizing effect of water was evident in all samples, with the pullulan, blend and bilayer films exhibiting greater glass transition temperature ( $T_g$ ) depression than the plain sodium caseinate films at similar moisture content levels. This differentiation was attributed to structural variation between the two polymers. Sorbitol addition decreased the  $T_g$  of both polymers at water contents up to 10% w/w; however, at higher hydration levels sodium caseinate exhibited an increase in  $T_g$  in contrast to pullulan, which showed a continuous decline. The apparent activation energy  $E_a$  of the primary relaxation ( $\alpha$ -relaxation) decreased with increasing moisture and sorbitol content. In all sorbitol-plasticized films, a low-temperature relaxation ( $\tan \delta$  peak) observed in the region of  $T_g$  of sorbitol, shifted to lower temperature with increasing moisture content; the intensity of this transition increased with increasing sorbitol content and the corresponding  $E_a$  values were similar to those of a primary relaxation. The low-temperature transition might originate from a coupling of  $\beta$ -relaxation of the polymer and the  $\alpha$ -motions of sorbitol. The fragility parameter,  $m$ , was calculated for all systems and allowed their characterization as relatively strong materials according to Angell's classification; the fragility decreased with increasing water content. The time–temperature superposition principle, using the Williams–Landel–Ferry equation, applied successfully to plain polymer films as well as to blends and bilayers, assuming that the  $C_1$  and  $C_2$  constants do not take their universal values, but are optimized for each system separately.

© 2006 Elsevier Ltd. All rights reserved.

**Keywords:** Pullulan; Sodium caseinate; Edible films; Calorimetry; Thermomechanical analysis; Water sorption; Sorbitol; Plasticization

## 1. Introduction

Over the past decade, food scientists have been increasingly interested in the development of edible films and coatings made of biopolymers such as polysaccharides and proteins or their blends. Particularly, the combination of such ingredients is an effective method to improve the

performance of the films owing to their variability in physical properties and/or their interactions. However, the compatibility of blend components is an important issue when dealing with mixtures of biopolymers as this might drastically alter the performance of these materials (Diab, Biliaderis, Gerasopoulos, & Sfakiotakis, 2001).

Pullulan is a water-soluble microbial polysaccharide extracellularly produced by the fungus-like yeast, *Aureobasidium pullulans* (Yuen, 1974). It consists of maltotriose units interconnected via  $\alpha$ -(1→6) linkages (Yuen, 1974), that are responsible for the irregularly ordered chains and

\*Corresponding author. Tel.: +30 2310 471467/991716; fax: +30 2310 471257.

E-mail address: [biliader@agro.auth.gr](mailto:biliader@agro.auth.gr) (C.G. Biliaderis).

for the ensued amorphous character of this polysaccharide (Gidley, Cooke, & Ward-Smith, 1993). This polysaccharide is an excellent edible film former; its films are colorless, tasteless, odourless, transparent, flexible, highly impermeable to oil and oxygen and heat-sealable (Yuen, 1974). A series of recent papers (Biliaderis, Lazaridou, & Arvanitoyannis, 1999; Lazaridou & Biliaderis, 2002; Lazaridou, Biliaderis, & Kontogiorgos, 2003) on the thermomechanical properties of pullulan alone and its blends with different polysaccharides, such as starch and chitosan added up to a more complete characterization of this biopolymer that, despite of its interesting properties, is not extensively exploited. On the other hand, caseinates are generally accepted as non-ordered polymers, containing mostly random coil chain segments (Siew, Heilmann, Eastal, & Cooney, 1999). Consequently, sodium caseinate readily forms films owing to its high water solubility, its random-coil nature and the capacity to form chain aggregates via electrostatic, van der Waals forces and hydrophobic interactions (McHugh & Krochta, 1994).

The physical properties of biopolymers are dependent on temperature, moisture content as well as time. Water and/or low molecular weight co-solute (e.g. polyol) plasticization is typical for polysaccharides and proteins due to their hydrophilic nature; i.e. their glass transition temperature ( $T_g$ ) strongly decreases with increasing water content. The plasticization action of water and/or polyols on food materials has been extensively reported in the literature (Biliaderis et al., 1999; Bizot, Le Bail, Leroux, Roger, & Buleon, 1997; Cherian, Gennadios, Weller, & Chinachoti, 1995; Diab et al., 2001; Gaurdin, Lourdin, Le Botlan, Ilari, & Colonna, 1999; Gontard, Guilbert, & Cuq, 1993; Kalichevsky & Blanshard, 1993; Kalichevsky, Blanshard, & Tokarczuk, 1993; Lazaridou & Biliaderis, 2002; Lazaridou et al., 2003; Lukasik & Ludescher, 2006; Moates, Noel, Parker, & Ring, 2001; Myllärinen, Partanen, Seppälä, & Forssell, 2002; Slade & Levine, 1991, 1993). Therefore, studying the plasticizing action of water and/or other co-solutes on food biopolymers and the glass transition phenomena related with such systems is of major importance for the prediction and understanding the functional behavior and stability of food components during processing and storage of food systems.

Moreover, studying of biopolymer blend properties is important in the context of exploring different ways for preparation of biopolymer films with versatile and improved characteristics. On the other hand, layered films, owing to a different morphology, which allows component interactions only at the interface, offer an interesting comparison with blend systems made of the same biopolymers.

The aim of the present work, therefore, was to investigate on a comparative basis the thermo-mechanical properties of an amorphous polysaccharide (pullulan) and a non-ordered protein (sodium caseinate) as well as of their blend and bilayer systems as affected by water and sorbitol added as co-plasticizer.

## 2. Materials and methods

### 2.1. Materials

Pullulan was a food grade preparation from Hayashibara Biochemical Laboratory, (Okayama, Japan). Sodium caseinate was from Wako Chemicals (Japan) and sorbitol (analytically pure) was obtained from Sigma Chemical (St. Louis, MO, USA). Inorganic salts (reagent grade) used for adjusting the relative humidity (saturated salt solutions) were from Merck KgaA (Darmstadt, Germany). Silica gel used as desiccant was purchased from Sigma-Aldrich GmbH (Germany).

### 2.2. Sample preparation

Pullulan, sodium caseinate as well as their mixture in a ratio of 1:1 (w/w) were dissolved in distilled water under continuous stirring to obtain casting solutions of either 4% (w/w) concentration for determination of the moisture sorption isotherms or 7.5% (w/w) for preparing specimens for differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). The polyol-containing samples were prepared by adding sorbitol (15 or 25% dry basis (db)) to the polymer solutions. The solutions were then filtered through a coarse glass filter to remove any unsolubilized material (usually less than 0.5% of the dry initial matter), vacuum degassed to remove air bubbles and cast on plastic frames. They were subsequently stored in an oven at 35 °C allowing them to dry slowly. Bilayer films were prepared by successively casting of sodium caseinate solutions onto already preformed pullulan films.

### 2.3. Moisture sorption isotherms

Film samples (~300 mg) were placed in previously weighed aluminum dishes and dried at 45 °C in an air-circulated oven over silica gel for 3 days. Then samples were subsequently kept in desiccators over saturated salt solutions of known relative humidity (RH) at 25 °C for 21 days, a time sufficient to reach constant weight and hence practical equilibrium. The desired RH conditions were reached by using the following salt solutions: LiCl,  $\text{MgCl}_2 \times 6\text{H}_2\text{O}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ ,  $\text{NaNO}_2$ , NaCl, KCl and  $\text{KNO}_3$  which give  $a_w$  values of 0.11, 0.33, 0.43, 0.53, 0.64, 0.75, 0.84 and 0.94, respectively (Rockland, 1960). The moisture content of samples, after storage, was determined by drying at 110 °C for 2 h. The obtained data were fitted to the Brunauer–Emmett–Teller (BET) or Guggenheim–Anderson–DeBoer (GAB) sorption isotherm models.

The BET model is given by

$$\frac{a_w}{(1 - a_w)m} = \frac{1}{m_m K} + \left[ \frac{K - 1}{m_m K} \right] a_w,$$

where  $m_m$  is the BET monolayer value, and  $K$  is a constant. The constants  $m_m$  and  $K$  were calculated from the linear

Download English Version:

<https://daneshyari.com/en/article/606012>

Download Persian Version:

<https://daneshyari.com/article/606012>

[Daneshyari.com](https://daneshyari.com)