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Effect of sodium acetate and drying temperature on physicochemical and thermomechanical properties of gelatin films

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ABSTRACT

The aim of this work was to evaluate the effect of sodium acetate (NaOAc) on the physicochemical properties of gelatin films with different leveling of triple helical structure. Films were obtained by casting method and dried at two temperatures (25 and 35 °C). Drying at 25 °C improved physical properties and increased the formation content of triple helix. The plasticizing effect of NaOAc was shown from typical stress–strain curves with the features of ductile materials. Dynamic mechanical thermal analysis (DMTA) also confirmed the thermomechanical properties of the films and revealed the decrease of glass transition temperature (T_g) with increasing NaOAc content. The increase of moisture content or decrease in intermolecular forces because of the existence of NaOAc might be attributed to the plasticizing effect. Films with NaOAc showed a higher capacity to absorb water compared to those without NaOAc at higher relative humidity (75% and 97%). All these gelatin films exhibited dominant elastic behavior (than viscous behavior) over the entire frequency range (0.1–100 Hz) at any loading content of NaOAc but the compactness of films was changed. X-ray diffraction (XRD) and water contact angle (WCA) revealed that the NaOAc crystals were dissolved in the gelatin matrix. These results may cause the extensive concern for the effects of salts (organic or inorganic) on films because salts exist widely.

1. Introduction

Gelatin is one of the most popular biopolymers and it's obtained by a controlled degradation of the fibrous insoluble collagen which is widely present in nature as the major constituent of bones, connective tissue and skin (Karim & Bhat, 2009; Schrieber & Gareis, 2007). For many years, gelatin has been widely used in food, pharmaceutical, and photographic industries. Common industrial applications are coatings for food products, gel desserts, microencapsulation, hard and soft capsules, sealants for vascular prostheses, as well as wound dressing and adsorbent pad for surgical use (Bigi, Cojazzi, Panzavolta, Rubini, & Roveri, 2001; Bigi, Panzavolta, & Rubini, 2004). Gelatin from various sources (mammalian and fish) has gained extensive attention as a film-forming material because of its gelling properties and hence excellent film-forming ability (Arvanitoyannis, Psomiadou, Nakayama, Aiba, & Yamamoto, 1997; Gómez-Estaca, Gómez-Guillén, Fernández-Martín, & Montero, 2011; Jeya Shakila, Jeevithan, Varatharajakumar, Jeyasekaran, & Sukumar, 2012).

Collagen has a triple-helix structure stabilized mainly by the formation of inter-chain hydrogen bonds between carbonyl and amines groups. Although the composition of gelatin is closely similar to that of the collagen, the triple helix of gelatin is broken and a coil configuration composed of single random chains is obtained after the hydrolysis process (Rivero, García, & Pinotti, 2010; Staroszczyk, Pielichowska, Sztuka, Stangret, & Kołodziejska, 2012). However, the polymer chains can undergo a conformational coil-helix transition by reducing the temperature of the gelatin solution. Generally, gelatin films cast below their gelation temperature, gelatin solution can form partially collagen-like triple helical structures, thus the triple helix can lock in the film matrix as water evaporates. This type of gelatin films is usually referred to as "cold-cast gelatin films". On the contrary, less triple helical structures can be obtained for films cast above gelation temperature. In this case the films might remain in a primary random coil conformation and they are referred to as "hot-cast gelatin films" (Badii, MacNaughtan, Mitchell, & Farhat, 2014; Chiou et al., 2009; Chiou et al., 2008). Usually, gelatin from bovine or pig has a higher gelation

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temperature than that from fish, especially that from cold-water species. This is mainly due to mammalian gelatin having higher concentrations of imino acids (Chiou et al., 2009). Moreover, the mechanical properties of gelatin films were highly related to the triple helix content of gelatin (Bigi, Bracci, Cojazzi, Panzavolta, & Roveri, 1998; Bigi et al., 2004). Greater tensile strength and elongation at break were observed in cold-cast than hot-cast gelatin films (Chiou et al., 2009). This means that superior mechanical properties were related to greater amount of triple helix structure. In addition, mammalian gelatin commonly has better physical properties as well as greater thermal stability than most fish gelatin, and this has been also related mainly to their higher imino acid content (Gómez-Estaca, Montero, Fernández-Martín, Alemán, & Gómez-Guillén, 2009). It is generally recognized that the imino acids (proline and hydroxyproline) are important in the renaturation of triple helical structure during gelling (Muyonga, Cole, & Duodu, 2004).

Acetic acid and sodium acetate often act as buffers to keep a relatively constant pH level. This is useful especially in biochemical applications where reactions are pH-dependent in a mildly acidic range. Sodium acetate (NaOAc) can be produced via many methods but mainly through the reaction of acetic acid and sodium carbonate or sodium hydroxide. This process is very common in applications that involve chitosan because of its inability to dissolve in water. Acetic acid solution is used frequently because it protonates the amines converting the polysaccharide to a polyelectrolyte (Jeya Shakila et al., 2012). It is necessary in many of applications of chitosan to adjust the pH to higher values (4–6). Such applications are polymer blending between chitosan and gelatin (Pereda, Ponce, Marcovich, Ruseckaite, & Martucci, 2011) and chitosan nanoparticles production through mechanisms of ionic gelation with polyanions (Hu, Wang, Li, Zeng, & Huang, 2011; Rampino, Borgogna, Blasi, Bellich, & Cesaro, 2013). In those cases sodium hydroxide is often used to adjust the pH resulting in the formation of NaOAc. In addition, our previous experimental results showing that when the pH value of pullulan-chitosan composite solution was increased from 3 to 5, the tensile strength of pullulan-chitosan blended film decreased while the elongation at break increased. Similar results were also obtained in our lab when increased the pH of gelatin-chitosan solution from 3.5 to 4.5. Generally, it is well known that the content of NaOAc increased when increased the pH of acetic acid solution.

NaOAc is commonly used as a food preservative. It has the ability to suppress the growth of food-borne bacteria and protect against food deterioration. It is also used for regulating the acidity or alkalinity of food products. Sodium acetate and sodium diacetate are used frequently as flavor enhancers in bread, cakes, cheese and snack food. Furthermore, it is widely available, economical, and generally "recognized-as-safe" (Ghomi et al., 2011; Sallam, 2007). Antimicrobial ability of different percentages of NaOAc in various meat and seafood has been previously reported (Yesudhason, Lalitha, Gopal, & Ravishankar, 2014). However, direct application of antimicrobial substances, such as dipping, spraying or brushing, may result in the inactivation or evaporation of active agents and rapid migration into the bulk of the foods. Controlling surface microbial growth on food is important because it is the main source of contamination for many chilled food products. Therefore, an appropriate way is to incorporate an antimicrobial agent into biobased edible films. Manju, Jose, Srinivasa Gopal, Ravishankar, and Lalitha (2007) and Yesudhason et al. (2014) have reported that combination of packaging and NaOAc extended the shelf life and quality of fish at refrigeration temperatures.

In the present study, we investigated the influence of NaOAc on the physicochemical and thermomechanical properties of gelatin films. The sol-gel and gel-sol transition temperature of gelatin was determined by dynamic viscoelastic measurements and differential scanning calorimetry (DSC), respectively. Two different drying temperatures (25 °C and 35 °C) were used to obtain gelatin films. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) were used to determine the triple helix content. It is, to our knowledge, the first study on the effects of NaOAc on edible films. The existing state of NaOAc in the gelatin matrix was investigated as well as the effect of water activity on the isothermal water absorption of gelatin films with and without NaOAc.

2. Materials and methods

2.1. Materials

Gelatin (type B) and sodium acetate (NaOAc) were purchased from China Medicine (Group) Shanghai Chemical Reagent Corporation (Shanghai, China). All other reagents were of analytical grade.

2.2. Film forming solution preparation

Gelatin solution was prepared at concentration of 4% (w/v) by hydrating gelatin powders in distilled water for 1 h at room temperature. The solution was then heated at 65 °C with continuous stirring in a magnetic stirrer until complete dissolution. Sodium acetate was obtained at concentration of 0.7% (w/v) by dissolving NaOAc powder in distilled water.

2.2.1. Dynamic viscoelastic properties

Dynamic viscoelasticity of the gelatin solution was carried out on a rheometer (AR-G2, TA Instruments, USA) using a plate–plate geometry (diameter of 60 mm, gap of 1 mm). Cooling from 37.5 to 17.5 °C took place at a scan rate of 0.1 °C/min, a frequency of 1 Hz, and a target strain% of 0.5%. The storage modulus (G', Pa), loss modulus (G'', Pa) were recorded as a function of temperature. Gelation temperature was determined from where G' and G'' intersect with the linear temperature gradient.

2.2.2. Differential scanning calorimetry (DSC) measurements

The melting behavior of gelatin gel was measured by a differential scanning calorimeter (DSC) (Netzsch DSC 204 F1, data processor Proteus® Software, Germany) according to the method of (Yoshimura et al., 2008). A 50 μL portion of gelatin solution was sealed in a 70 μL stainless steel cell and incubated at 4 °C for 48 h to gel and then scanned from 20 to 40 °C at a heating rate of 1 °C/min. From the DSC curve, the helix-coil transition temperature was calculated as the temperature where the endothermic peak occurs.

2.3. Film preparation

Casting/solution evaporation method was used in this study for preparing films. NaOAc solution was obtained at 0.7% w/v and

Table 1
Composition of film-forming solutions. Gelatin solution used for film preparation was 50 mL at concentration of 4% (w/v) in all films.

NaOAc/Gelatin mass ratio	NaOAc (mL)	Water (mL)
0%	0	50
5.25%	15	35
8.75%	25	25
10.5%	30	20
12.25%	35	15