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Study of the influences of film processing conditions and glycerol amount on the water sorption and gas barrier properties of novel sodium caseinate films

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ABSTRACT

This study deals with water sorption characteristics and gas barrier properties of sodium caseinate based edible films as a function of processing type and processing additives. Two processing routes are adopted: solution casting and blown-film-extrusion. Two processing additives are used: glycerol as plasticizer and ethanol as protein denaturing agent. It is shown at first that the water and gas transport properties are neither affected by the processing technology nor by the use of ethanol during the fabrication step.

Water sorption and thermal properties of blown films prepared for glycerol contents varying from 15 to 25 wt% are then studied for a wide range of relative humidity. The determination of the water sorption isotherms and their modeling by Park's equation as well as the study of the water sorption kinetics parameters allow discussing the sorption mechanisms as a function of the respective plasticizing effect of glycerol and water, on one hand and of the ability of water molecules to form clusters within the material, on the other hand. The decrease of the glass transition temperature values of the films as a function of increasing water content is analyzed thanks to Gordon–Taylor equation and it is related to the respective plasticizing role of glycerol and water, as evidenced from water sorption analysis.

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1. Introduction

Over the past decades, packaging industry generates an increasing interest for biopolymer films in order to reduce the environmental impact of plastic waste mainly produced by its huge application area. In this context, edible films provide, thanks to their functional properties and biodegradable nature, the double advantage of decreasing the quantity of conventional plastics used in the complex packaging systems and of minimizing or even removing the environmental impact of packaging material [1].

Protein based edible films with their good gas barrier properties are promising materials for packaging applications [2]. Food

researchers are aware of high potential persisted in the utilization of these films, thus they had been studied extensively [1,3–5]. Despite numerous advantages reported, protein based edible films are still not able to take place concretely in the market. The only satisfying explanation to their current status is drawbacks related to their poor mechanical properties, hydrophilic nature [6–9] rendering films very moisture sensitive and adopted fabrication process [10], solvent cast process, which is not adapted to industry for financial and ecological reasons. Thus it is still necessary to develop flexible free-standing edible films by commonly used plastic transformation technologies such as extrusion.

Sodium caseinate is a water-soluble polymer obtained by the acid precipitation and then neutralization of casein, the major bovine milk protein [6]. It has high nutritional value, excellent film forming properties due to its random coil structure and good oxygen barrier properties which makes it a very attractive candidate for edible film making [11,12]. Lately sodium caseinate based edible films produced by conventional plastic technologies, blown-film extrusion, has been reported by Belyamani et al. [13]. A continuous production of these films by industrial methods may

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lead to new opportunities and encourage their commercialization. Some extra data is still needed on physical properties of sodium caseinate based blown films in order to determine their limits of use as edible food packaging films. Furthermore, it is important to study their performances in comparison with those of solution casting films to find out if there is any influence of thermo-mechanical processing.

In the first part of this paper, water and gas transport properties of sodium caseinate films obtained by solution casting and by extrusion, respectively were studied and compared. Ethanol which is well known as a denaturing agent for most proteins is added as solvent in film-forming solutions. It also has an important role in ionization level of caseins and affects the dissolution process of sodium caseinate in water [14]. Gontard et al. [15] reported the decreasing water vapor barrier properties of gluten based edible films with increasing ethanol concentration in the film-forming solution. In the present study, ethanol was used to facilitate the extrusion of sodium caseinate. Its influence was also investigated on the water vapor diffusivity. Later, the impact of the use of glycerol as plasticizer in the material was analyzed. This part was mainly focused on the water sorption properties of glycerol-plasticized films because absorbed water may greatly alter mechanical and barrier properties of hydrophilic materials under real usage conditions of packaging films. Although GAB and BET equations are the models commonly used by authors [13,16–19], in this work for the first time, to our knowledge, Park's equation was used for modeling the sorption isotherms of sodium caseinate films. This model offers a detailed description of sorption phenomena in the whole range of water activity. In addition to all, a detailed study on sorption kinetics and thermodynamic characteristics of these films were proposed.

The originality of this work persists mainly in the fabrication process of films. It focuses on water sorption and oxygen and water permeation properties of sodium caseinate blown films with a fundamental approach. This permitted relating theoretical transport phenomena of small molecules through thin films to marketable films' final properties.

2. Experimental

2.1. Materials

Sodium caseinate native powder was purchased from EPI Ingredients (Ancenis, France). Glycerol was obtained from Sigma Aldrich (St Louis, MO) and ethanol 96°, used as denaturizing agent, was supplied by Carlo Erba reagents (Val de Reuil, France).

2.2. Films preparation

Thermoplastic sodium caseinate films were prepared using two different processing routes: blown extrusion process and solvent cast process. For the blown extrusion film process, in a first step, sodium caseinate pellets were elaborated using a twin-screw extruder from Clextal (Clextal BC 21, France) as described previously by Belyamani et al. [13]. The sodium caseinate powder was introduced without any treatment into the first zone of the extruder. Glycerol and water were used as food-grade plasticizer agents and alimented into the 2nd zone using a piston pump (PCM pumps, PP9, France). In the case of ethanol addition, 20 mL of ethanol was added in 100 mL of water. A degassing zone permitted the solvents evaporation (water and ethanol) during the pellet production process (80 °C). Different amounts of glycerol were used: 15, 20 and 25 wt% and were expressed with respect to the total matter content. The obtained extrudates were pelletized after cooling at ambient atmosphere. The obtained pellets were then introduced in an extruder equipped with a small compression rate (2.5) screw with a diameter of 20 mm and a length-to-diameter ratio of 25. The screw speed was set to 45 rpm, and the barrel and the die were heated to 80 °C which was sufficient enough to melt the

thermoplastic pellets. The molten protein was forced through the vertical annular die of spiral mandrel type. The tube was pulled upwards from the die by a pair of nip rolls placed 1 m above the die, and the thickness of the film was controlled by the speed of the nip rollers. Residence times during twin-screw extrusion and blown-film extrusion processes were 2.5 and 7 min, respectively.

For the solvent cast process, the film preparation consisted in the dissolution of native sodium caseinate powder with or without glycerol in distilled water at a concentration of 15 w/v%. Two weight amounts of glycerol expressed with respect to the total matter content were used: 0 and 20. In the case of ethanol addition, 20 v/v% of ethanol was added to water. The solution was continuously stirred at room temperature for 2 h. After degassing, the solution was poured onto polystyrene plates and solvent evaporation was carried out at room temperature all night long. In following part of this manuscript, sodium caseinate films prepared by both processing routes will be denoted as NaCxGy: x being "ext" for blown extruded films and "sc" for solvent cast films and y indicating the total amount of glycerol in the film. If ethanol was used during the film process, NaCxGyEtOH was used as nomenclature. In all cases, the film thickness was measured by a micrometer (Elcometer Limited, Manchester, United Kingdom) and was approximately 70 µm whatever is the film process.

Fig. 1a and b represents sodium caseinate films prepared by thermoplastic process and solvent cast process, respectively.

2.3. X-ray diffraction (XRD)

The X-ray diffraction (XRD) analyses were performed with a Bruker D8 Advance diffractometer (Villeurbanne, France). All spectra were recorded at room temperature in the range of 2θ between 1° and 30° by step of 0.02°. Thin films cut into 20×20 mm² dimensions were previously conditioned in an environmental chamber ensuring 60% of relative humidity (RH) at 25 °C. Samples at equilibrium state were spread on neutral mono substrates and fixed with an adhesive tape by sides out of the analyzed area. For the different films, the intensity values were normalized taking into account the real thickness of the films.

2.4. Differential scanning chromatography (DSC)

Differential scanning chromatography (DSC) analyses were carried out using a DSC QA 10 (TA Instruments). Samples were either conditioned at 65% RH and 80% RH at 25 °C in an environmental chamber, or dried in a vacuum oven. In each case, samples were analyzed after the equilibrium state was reached. Conditioned samples (weigh between 3 and 4 mg) were sealed in hermetic aluminum pans. A ramp of temperature from 20 °C to 120 °C with a constant speed rate of 10 °C/min was employed. An empty aluminum pan was used as reference. Obtained data permitted to determine the glass transition temperature T_g of the different films by TA Universal Analysis software (TA Instruments, New Castle, USA).

2.5. Dynamic vapor sorption (DVS)

Dynamic vapor sorption analyzer, DVS Advantage, was used to determine water sorption isotherms of the different samples. The vapor partial pressure was controlled by mixing dry and saturated nitrogen, using electronic mass flow controllers. The experiments were carried out at 25 °C. The initial weight of the sample was approximately 30 mg. The sample was predried in the DVS Advantage by exposure to dry nitrogen until the dry mass of the sample was obtained (m_0). A partial pressure of vapor (p) was then established within the apparatus and the mass uptake (m_t) was followed as a function of time (t). The mass at equilibrium (m_{eq}) was considered to be reached when changes in mass with time (dm/dt) were lower than 0.0002 mg min⁻¹ for at least five consecutive minutes. Then, vapor

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