Journal of Food Engineering 121 (2014) 39–47

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Production and characterization of sodium caseinate edible films made by blown-film extrusion

Imane Belyamani *, Frederic Prochazka, Gilles Assezat

Université de Lyon, F-42023 Saint Etienne, France
CNRS, UMR 5223, Ingénierie des Matériaux Polymères, 42023 Saint Etienne, France
Université de Saint Etienne, Jean Monnet, F-42023 Saint Etienne, France

ARTICLE INFO

Article history:
Received 3 May 2013
Received in revised form 3 August 2013
Accepted 9 August 2013
Available online 22 August 2013

Keywords:
Sodium caseinate
Edible film
Food packaging
Twin-screw extrusion
Blown-film extrusion

ABSTRACT

Caseinates are considered as an interesting raw material for making biodegradable and water-soluble packaging. However, the development of plasticized caseinates, especially sodium caseinate, has mainly focused on the formation of films obtained by solution casting. This process, consisting in drying aqueous caseinate–plasticizer solutions spread on a hydrophobic plate, is not adapted to an industrial scale production. In the present study, a co-rotating twin-screw extruder was used to produce glycerol plasticized caseinate pellets. These transparent, homogenous, smooth pellets were transformed into thin films using a classical film blowing machine. Mechanical properties of the thermoplastic material have been measured as a function of glycerol content and environmental relative humidity and found to be greatly affected by glycerol and moisture levels. Water vapor permeability (WVP) of blown films was also investigated as a function of glycerol concentration, and it showed that the higher the glycerol content is, the lower the resistance to water transfer is. The obtained extruded sodium caseinate films are transparent, handleable and can even be edible. Several applications of these materials in food or non-food packaging could be developed.

1. Introduction

Proteins are attractive for biodegradable materials field as they possess a wide range of chemical functionalities (Petersen et al., 1999). They are based on 20 amino acid monomers; each one has a different side group that lends to it unique character (Krochta, 2002). This results in many possibilities of bindings and structures, and in complex and varied properties (Rouilly and Rigal, 2002). These characteristics make proteins excellent candidates for the development of bio-based and biodegradable packaging in order to improve food product shelf life and food quality.

Soy protein (Brother and McKinney, 1939; Brandenburg et al., 1993; Guerrero et al., 2010; Kunte et al., 1997; Kumar et al., 2002; Kurose et al., 2007; Kumar and Zhang, 2009; Lodha and Netravali, 2005; Otaigbe and Adams, 1997; Sue et al., 1997; Schilling et al., 1995; Wang et al., 1996; Zhang et al., 2001), wheat gluten (Anker et al., 1972; Fischer, 2004; Li and Lee, 1996; Micard et al., 2000; Redl et al., 1999a,b), corn zein (Ha and Padua, 2001; Lawton, 2004; Padua and Wang, 2002), collagen protein (Chirita, 2008; Deiber et al., 2011; Goissis et al., 1999; Ho et al., 2001; Maser et al., 1991; Sionkowska, 2000) and gelatin protein (Achet and He, 1995; Bigi et al., 1998, 2000, 2001; Cutter, 2006) have been studied for many years to make edible and/or biodegradable films and they were reported to be innovative materials for packaging. Among these proteins, casein, the major protein component of milk, constitutes an interesting and a suitable raw material for making bioplastics. It represents 75–80% of all milk proteins and it is organized on a micellar structure which consists of α, β and κ-casein as shown in Fig. 1 (Cayot and Lorient, 1998; Kinsella, 1984).

Due to their low secondary structures (alpha-helix and beta-sheets), caseins are random coil polypeptides with a high degree of molecular flexibility and thus able to form typical intermolecular interactions (hydrogen, electrostatic and hydrophobic bonds) (Kinsella, 1984; Swaisgood, 1982). With these properties, caseins can easily form films without further treatment (Lacroix and Cooksey, 2005). Caseinates are produced by adjusting acid-coagulated casein to pH 6.7 using sodium, calcium or potassium hydroxide (Cayot and Lorient, 1998; Kinsella, 1984).

Research on plasticized casein, especially sodium caseinate, has mainly focused on the formation of films obtained by solution casting. This process consists in drying aqueous caseinate–plasticizer solutions spread on a hydrophobic plate (Arrieta et al., 2013; Avena-Bustillos and Krochta, 1993; Audic and Chaufer, 2005, 2010;

* Corresponding author. Address: School of Polymers and High Performance Materials, University of Southern Mississippi, 118 College Drive #5050, Hattiesburg, MS 39406, United States. Tel.: +1 601 310 2734.
E-mail address: imane.belyamani@gmail.com (I. Belyamani).

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http://dx.doi.org/10.1016/j.jfoodeng.2013.08.019

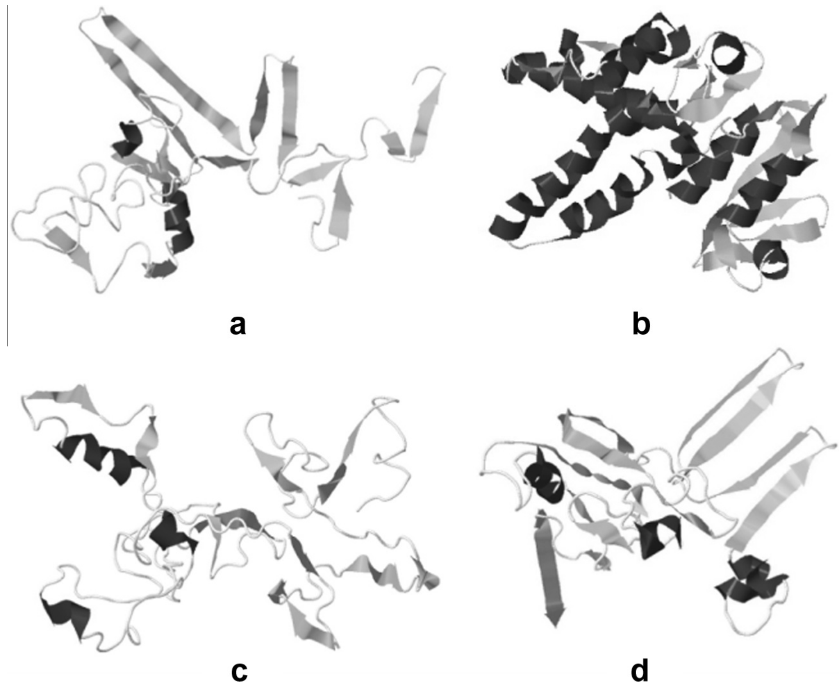

Fig. 1. Three-dimensional molecular model for the predominant caseins in cow milk: (a) α_{s1}-casein (Kumosinski et al., 1994), (b) α_{s2}-casein (Farrell et al., 2009), (c) β-casein (Kumosinski et al., 1993a) and (d) κ-casein (Kumosinski et al., 1993b).

Barreto et al., 2003; Broumand et al., 2011; Chen, 2002; Gialamas et al., 2010; Khwaldia et al., 2004; Siew et al., 1999; Schou et al., 2005).

Caseinates based films show hydrophilic properties due to their high amount of polar groups that provide excellent barriers to non-polar substances such as oxygen, carbon dioxide and aromas (Audic et al., 2003). However, it was reported to be an ineffective moisture barrier, as expected for hydrophilic materials (Guilbert, 1986; Krochta et al., 1990).

Plasticizers are added to enhance workability, elasticity and flexibility of the film. Plasticization occurs in the higher molecular-mobility amorphous region, and the ability of plasticizers to interrupt hydrogen bonding along the protein chains depends on the amount and type of the plasticizer (Sothornvit and Krochta, 2005). Siew et al. (1999) have reported that the plasticizer content has a large impact on film mechanical properties. They have shown that increasing glycerol content in the sodium caseinate films reduces their tensile strength and increases the elongation at break. As with other proteins films, glycerol is the plasticizer commonly used for caseinates based films. Audic and Chaufer (2005) and Siew et al. (1999) have demonstrated that sodium caseinate plasticized with glycerol has good mechanical properties as compared to those plasticized with polyethylene glycol (PEG) and other polyols.

The solution-casting method is only adequate for laboratory use; it cannot be applied in a large scale production of films that could be used for packaging, food wraps or pouches. Therefore, more efficient techniques are needed for commercial film production. Extrusion process would be an interesting process in increasing the commercial potential of biodegradable films, offering several advantages over solution-casting. Extrusion can result in a highly efficient manufacturing method with commercial potential for large-scale production of edible films due to the low moisture levels, high temperatures, and short times used (Hernandez-Izquierdo and Krochta, 2008). It is a continuous process where the raw materials are continuously introduced into a hopper, conveyed by a screw and pushed through a die of a desired shape. This process involves several operations at the same time: melting, mixing, kneading, stretching and conveying (Hernandez-Izquierdo et al., 2008). These characteristics often result in films with improved mechanical, barrier, and microstructural properties (Hernandez-Izquierdo and Krochta, 2008). Extruders have been used successfully in the production of protein based films, and were found to have a significant effect on material properties. For instance, Ha and Padua (2001) have reported that the higher pressure and the shearing force that can be developed in twin-screw extrusion increase the tensile strength of the extruded zein resins based sheets. On the other hand, Pommet et al. (2003) have demonstrated that the properties of extruded wheat gluten can be tuned for a wide range of applications by changing the thermoplastic processing conditions (temperature and/or shear) to obtain the desired structure.

To date, sodium caseinate based edible film has been manufactured using solution-casting method only. Extrusion process would be a highly efficient method for the continuous shaping of thermoplastic plasticized caseinate. Therefore, using extrusion to produce sodium caseinate films is a real novelty that could present the opportunity to scale-up the transformation of caseinate biodegradable/edible materials, and to our knowledge, has never been performed before.

The objectives of the present study are: (a) to demonstrate that sodium caseinate could be transformed by the processes used for synthetic plastics industry: twin-screw and blown film extrusion, and (b) characterize the thermoplastic caseinate materials and blown films in terms of mechanical properties and water vapor permeability.

2. Materials and methods

2.1. Materials

Sodium caseinates were purchased from Brenntag, France. It contained more than 88% proteins (dry basis), approximately 5%