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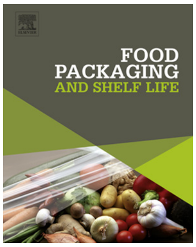

Mechanical and barrier properties of extruded film made from sodium and calcium caseinates

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ABSTRACT

Over the past few years, much interest has been placed into the investigation of increased barrier and mechanical properties of protein films via a multitude of approaches. Generally, these techniques involve modifications of interactions among protein molecules, such as ionic crosslinking using divalent ions. To evaluate the crosslinking effect of Ca^{2+} cations, films were made from calcium caseinate (CaCAS) and/or sodium caseinate (NaCAS). The production of caseinate thin films was carried out in two steps: first thermoplastic pellets were made using a co-rotating twin-screw extruder, then they were transformed into thin films (60 μm) using a classical film blowing machine. Tensile measurements were carried out at 60% relative humidity (RH) and 30 °C using a homemade testing machine which allows the change in environmental conditions during the test. The films mechanical resistance was found to be affected by the presence of Ca^{2+} ions; films made from CaCAS were rigid and less flexible than those based on NaCAS only. Water vapour permeability (WVP) and water diffusion were also measured. The reported data showed that films with only CaCAS or in mixture with NaCAS are less permeable to water vapour than those totally made from NaCAS. Likewise, the calcium ions were found to slow down the water diffusion.

Films based on CaCAS only or in mixture with NaCAS appear to be more attractive for food packaging, and their applications could be extended to other packaging area.

1. Introduction

Increasing interest in reducing packaging waste has encouraged the development and the study of biodegradable films based on proteins as degradable and renewable polymers. Casein-based edible films are attractive for food applications due to their high nutritional quality, excellent sensory properties, and good potential to adequately protect food products from their surrounding environment (Chen, 2002). The most commonly used form of casein in materials field is caseinates. Commercial caseinates are manufactured by dissolving fresh acid casein curd in sodium, calcium or potassium hydroxide followed by spray drying (Cayot &

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Lorient, 1998; Chen, 2002; Kinsella, 1984; Lacroix & Cooksey, 2005).

Caseinates have been studied for making edible and biodegradable films, and it was reported that they possess good film-forming and coating abilities. These properties are related to their open random coil structure and their ability to form typical intermolecular interactions (hydrogen, electrostatic and hydrophobic bonds) which increase inter-chain cohesion to form film (Audic, Chaufer, & Daufin, 2003; Chen, 2002; Kinsella, 1984; Lacroix & Cooksey, 2005; McHugh & Krochta, 1994; Swaisgood, 1982). However, caseinate based films are a poor moisture barrier because of their highly hydrophilic nature (Guilbert, 1986), which could limit their ability to provide desired functional properties.

Protein crosslinking approaches were attempted to enhance mechanical properties and resistance to moisture transfer of protein based films to make them as close as possible to the available packaging films based on synthetic polymers. Protein crosslinking refers to the formation of covalent bonds between polypeptide chains within a protein (intramolecular crosslinks) or between proteins (intermolecular crosslinks). Several techniques have been reported in the literature in order to achieve the casein crosslinking; enzymatic using transglutaminase (Motoki, Aso, Seguro, & Nio, 1987), chemical through the use of chemical agents such as formaldehyde or glutaraldehyde (Audic & Chaufer, 2010; Latha & Jayakrishnan, 1994.) and physical such as exposure to γ-irradiation (Audic & Chaufer, 2010; Brault, D'Aprano, & Lacroix, 1997; Lacroix, Jobin, Mezgheni, Srour, & Boileau, 1998; Ressouany, Vachon, & Lacroix, 1998) or to temperature (Abu Diak, Bani-Jaber, Amro, Jones, & Andrews, 2007), as low cost techniques. Another approach has involved the crosslinking effect of divalent calcium cations (Ca^{2+}). In fact, ionic calcium is known to form strong molecular crosslinking which tightens the protein matrix by limiting protein polymer segmental mobility (Avena-Bustillos & Krochta, 1993; Banerjee & Chen, 1995), and improves barriers and mechanical properties of edible films (Arrieta, Peltzer, Garrigos, & Jimenez, 2013). For instance, Banerjee and Chen (1995) reported that film made by casting calcium caseinate (CaCAS) solution was less permeable to water vapour and stronger than that made from sodium caseinate (NaCAS). On the other hand, Avena-Bustillos and Krochta (1993) concluded that treatment of NaCAS films with calcium chloride solution or calcium ascorbate buffer appeared to be more effective in reducing the water vapour permeability of films, compared to those made from CaCAS without further treatments. More recently, Fabra, Talens, and Chiralt (2010a) have reported that the substitution of NaCAS by CaCAS in CaCAS/NaCAS mixtures increases stiffness and resistance to break of the films.

This work follows up on a previous study (Belyamani, Prochazka, & Assezat, 2014) as to the feasibility of the transformation of NaCAS employing the processes used for synthetic plastics industry: twin-screw extrusion and blown film extrusion. The objective of the present work is to investigate the effect of the substitution of NaCAS by CaCAS in extruded NaCAS/CaCAS mixture on tensile properties, water vapour permeability, and resistance to liquid water transfer, as compared to the pure materials.

2. Materials and methods

2.1. *Materials*

Sodium and calcium caseinates were purchased from Brenntag (France). Both caseinates contained more than 88% proteins (dry basis), approximately 6% moisture, less than 0.15% lactose, and 1.25% Na^+ for NaCAS and 1.4% Ca^{2+} in the case of CaCAS. Glycerol was obtained from Sigma–Aldrich (France).

2.2. *Processing and characterization methods*

2.2.1. *Twin-screw extrusion*

The extrusion experiments were performed using a co-rotating twin-screw extruder from Clextral (Clextral BC 21, France) with 9 heating zones. Each zone was heated independently and cooled with recycled water. The interpenetrate screws had a length of 900 mm, a diameter of 25 mm, and the distance between screw's axe was 21 mm. A slit die of 4 mm diameter was used.

The NaCAS and CaCAS powders were mixed at the desired ratio before being introduced into the 1st zone using a K-Tron volumetric feeder (Ktron soder, Switzerland) while the glycerol and water were delivered separately into the 2nd zone using a piston pump (PCM pumps, PP9, France). The addition of water was used to control the shear viscosity of the melt, and then control the engine torque of the extruder. The screws were configured with conveying and kneading elements, and the barrel temperature along the screw ranged from 40 to 80 °C (Prochazka & Assezat, 2012). The setup was determined to denature the protein in order to increase the potential intermolecular interactions between the protein chain and the glycerol, and then increase the molecular flexibility. The obtained extrudates were pelletized after cooling. The glycerol rate was fixed at 20% (w/w, dry basis).

2.2.2. *Blown-film extrusion*

A blow-film extruder (Diani, Italy) with 5 zones was used for the production of thin films. The extruder consists of three zones and was 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. The thickness of the finished films averaged 60 μm and was measured using an electronic gauge (Mahr Federal, Millitron, Germany) with incertitude of 3 μm.

2.2.3. *Tensile tests*

Tensile measurements of blown films were performed using a homemade tensile test machine, which allows the change in environmental conditions (relative humidity and temperature) during the test. This measuring device is compact, with a sensitive force sensor, and measuring jaws for thin films were