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Effect of crystalline substances in biodegradable films

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A B S T R A C T

Films made of sodium caseinate and gelatine were prepared by casting method from a water solution containing glycerol as a plasticizer to obtain environmentally friendly and fully biodegradable materials for agricultural and packaging applications. Additionally, enzymatic protein cross-linking by microbial transglutaminase was applied. Potassium nitrate (KNO_3) was used as additive to investigate the influence of crystallization on the physical properties of protein films.

Mechanical properties (tensile strength and elongation at break) of the protein films were determined versus ratio of protein to potassium nitrate in the presence and absence of microbial transglutaminase. Furthermore, optical properties (film formation and consistency, surface texture, crystal size, shape, and distribution of incorporated potassium nitrate) were examined.

An increase of 122% and 177% in the elongation of the films was adopted due to the crystallization of KNO_3 in enzymatic-modified sodium caseinate and gelatine films, respectively. Pure sodium caseinate films distinguished ultimate tensile strengths of 4.95 MPa, while MTG-treated gelatine films achieved ultimate tensile strengths of 13.52 MPa. Altogether, the most appropriate overall mechanical performance was obtained for KNO_3/protein ratios of 1:6 in enzymatic-modified films.

Furthermore, an increasing content of crystalline KNO_3 results in increasing thickness, rough surfaces, decreased opacity, and whitish coloring of the films.

Keywords: Crystallization; Biodegradable films; Sodium caseinate; Gelatine; Potassium nitrate

1. Introduction

Today, the development of innovative materials to substitute synthetic polymers has become an important challenge. Among these materials are biopolymers from vegetable or animal proteins (Arvanitoyannis, 2006). These materials offer a unique set of properties that make them favorable for applications chiefly in market sectors such as packaging, agriculture, electronics, automotive, and medicine. Derived from natural sources, these biodegradable, biocompatible and non-toxic polymers meet the growing demands for environment-friendly products (Clarinval and Halleux, 2005).

In this study, biodegradable films and composites for agricultural applications (greenhouse, walk-in tunnel, low tunnel covers, and mulching) are in the focus. Petroleum-based plastics often remain undegraded after discard and a time-consuming and uneconomical recycling is unavoidable. The adoption of biopolymers avoids the removal of residual materials from the growing environment after functional compliance (Espi et al., 2006; Joo et al., 2005). Furthermore, degradation could offer additional benefit by controlling the release of incorporated agrochemicals, fertilizers and pesticides (Clarinval and Halleux, 2005).

The film forming and thermoplastic properties due to their abilities to form weak intermolecular interactions, i.e. hydrogen, electrostatic and hydrophobic bonds make, i.e. sodium caseinate a promising raw material for the production of biodegradable films and coatings (Audic and Chaufer, 2005).

However, for the majority of the mentioned applications, the improvement of the physicochemical properties

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of protein-based materials is of first importance. Therefore, chemical modifications of biopolymers and the development of specific additives (cross-linking agents and plasticizers) are already well investigated (Clarinval and Halleux, 2005).

Furthermore, an enzymatic catalyzed cross-linking of proteins associated with a controlled additive crystallization appears to be a promising way to improve physicochemical properties of biodegradable films and coatings. While the effects of transglutaminase treatment on the film properties of various proteins have been extensively studied the crystallization of selective additives in protein-based materials is a completely new approach for the optimization of the materials (Flanagan et al., 2003; Lorenzen, 2000; Oh et al., 2004; Tang et al., 2005; Wang et al., 2007; Yi et al., 2006).

Therefore, the objective of this study is to determine the influence of crystallized potassium nitrate on the mechanical and optical properties of sodium caseinate and gelatine films in the presence and absence of microbial transglutaminase.

2. Methods and materials

2.1. Materials

Sodium caseinate (NaCas) (protein 88%, fat 1.5%, lactose 0.2%, ash 4.5%, and water 6%) was provided by BMI e.G. (Landshut, Germany). Gelatine (high grade, type 280 bloom) was supplied by Gelita Europe (Eberbach, Germany). Microbial transglutaminase (MTG) (ACTIVA® WM, nominal activity = 100 U/g of powder) was purchased from Ajinomoto Europe Sales GmbH (Hamburg, Germany). Analytical grade glycerol and potassium nitrate were supplied by Carl Roth GmbH & Co. KG (Karlsruhe, Germany).

2.2. Film formation and preparation

Protein films were prepared by casting. An aqueous solution of sodium caseinate or gelatine (5%, w/w), glycerol (2.5%, w/w), and potassium nitrate (KNO_3) in different concentrations (KNO_3/protein ratios of 1:12 to 1:1.33) was magnetically stirred for 30 min at 90 °C in order to get a homogenous solution. For the addition of microbial transglutaminase (25 U/g NaCas) the solution was cooled to room temperature, the pH was set to 7 by adding 1 M sodium hydroxide (NaOH), and warmed up to 50 °C.

To prevent air entrapment in the films the solution was centrifuged for 1 min at 177 × *g* and 50 °C before the casting process. The film forming solution was spread onto a polytetrafluoroethylene (PTFE) plate and the film, dried for 48 h at room temperature and peeled off after the water evaporated. In order to provide homogeneous films in terms of thickness und surface conditions millimeter accurate screws were used to adjust the PTFE plates and to assure an equal wettability.

To ensure constant relative humidity (50 ± 2% RH) conditions the films were conditioned in a closed tank containing saturated solutions of $Ca(NO_3)_2 \cdot 4H_2O$ for at least 48 h at room temperature.

2.3. Mechanical properties

Mechanical properties (tensile strength and elongation) were measured according to the standard procedure of DIN EN ISO 527-3 using a material testing machine (BDO-FB0.5TH, Zwick/Roell, Ulm, Germany). Therefore the films were cut into test stripes with a wide of 15 mm and a length of at least 100 mm using a double-bladed roller knife. Film thickness was determined from the mean of three measurements across each specimen using a micrometer. Subsequently, the sample films were tested with a grip separation of 100 mm and a crosshead speed of 50 mm/min.

2.4. Film morphology

Optical properties (film surface, opacity, coloring, crystal size, shape, and distribution) were investigated using digital photography and light microscopy. Film samples were stored in a desiccator for at least 48 h to assure constant observation conditions. Micrographs were examined at magnifications of 5–335×.

2.5. Statistical analysis

Analysis of variance (ANOVA; Statistica® 8, StatSoft, Tulsa, OK, USA) was used to indicate a significant difference ($P < 0.05$) amongst the means. Five replications were employed for each sample.

3. Results and discussion

3.1. Film formation

Flexible, transparent, and light yellowish films with homogenous textures were obtained after drying the film-forming solutions containing NaCas and glycerol. Films made of gelatin showed transparent, homogenous, and non-sticky overall properties. The crystallization of the potassium nitrate due to the evaporation of the solvent results in increased film thickness, rough surfaces and increasing opacity.

3.2. Tensile strength

Tensile strength values of sodium caseinate in dependence of additive concentration and enzyme catalyzed cross-linking of the protein are given in Fig. 1.

The results for NaCas-films show a distinct dependence of the potassium nitrate concentration. The highest tensile strength of 4.95 MPa was achieved with pure NaCas-films

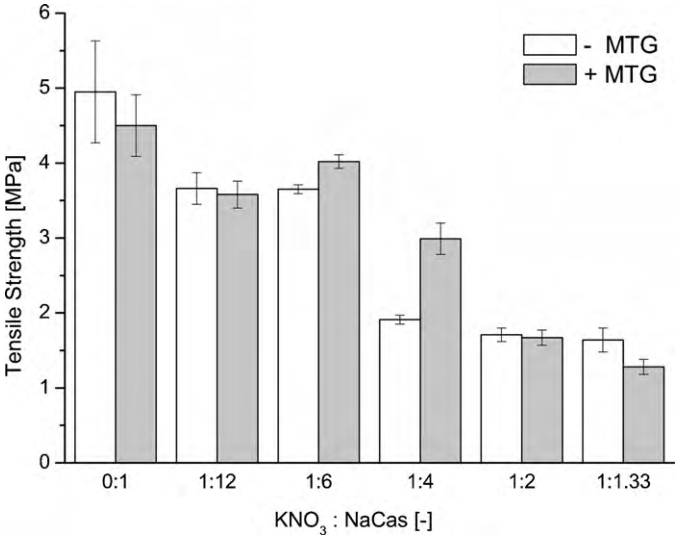

Fig. 1 – Tensile strength of MTG-treated (+MTG) and non-treated (−MTG) NaCas-films at different KNO_3 concentrations.