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Influence of plasticizers and crosslinking on the properties of biodegradable films made from sodium caseinate

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Abstract

Plasticized protein films were prepared by the casting method from water solution of sodium caseinate and plasticizers with the aim to obtain environmentally friendly materials for packaging applications. Mechanical properties (tensile strength, elongation and Young's modulus) of caseinate based films were determined versus ratio of protein to plasticizer, plasticizer type and relative humidity conditions. Among the different polyol-type plasticizers tested, glycerol (Gly) and triethanolamine (TEA) were the most efficient for the improvement of mechanical properties (high strains for low stresses). Further, chemical crosslinking between formaldehyde (HCHO) and free amino groups (ε-NH_2) of sodium caseinate was performed to increase water resistance of TEA plasticized films. Optimal mechanical properties, i.e. elastic modulus of 105 MPa, tensile strength of 8–9 MPa for elongation at break about 110–125% were obtained for HCHO/ε-NH_2 ratios higher than 1.35. Protein specific water solubility was determined from a 280 nm absorbance. For convenient crosslinker (HCHO) content sodium caseinate solubility can be lowered to less than 5 wt% after 24 h immersion in water.

Keywords: Sodium caseinate; Films; Crosslinking; Plasticization; Water solubility

1. Introduction

Sodium caseinate (NaCAS) is a commercially available water-soluble polymer obtained by acid precipitation of casein, the main protein in cow's milk (24–29 $g\,L^{-1}$). This natural polymer is composed of four major components [1], α_{s1}-CAS (38%), α_{s2}-CAS(10%), β-CAS (36%) and κ-CAS (13%) and a minor constituent, γ-CAS (3%) with molecular weights ranging from 19,000 to 23,900 $g\,mol^{-1}$.

Due to their renewable and biodegradable nature proteins are attractive for innovative uses and caseinate is of growing interest for "green" materials. Caseinate presents thermoplastic and film forming properties due to its random coil nature and its ability to form weak intermolecular interactions i.e. hydrogen, electrostatic and hydrophobic bonds [2,3]. These properties make sodium caseinate interesting raw material for several applications in substitution of traditional synthetic

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polymers. Considering their transparency, biodegradability and good technical properties (high barrier for gases like O_2) [4], caseinate based films can find applications in packaging [1,5], in edible or protective films and coatings [6,7] or in mulching films [8]. Such films are easily obtained from casting aqueous solutions of sodium caseinate.

The objective was to achieve caseinate based films with improved properties as close as possible to available packaging films based on synthetic polymers like polyethylene [7] or plasticized PVC [9]. Such films present good elongation at break (from 150% to about 400%) and a rather low tensile strength ranging from 20 to 30 MPa. However, compared to synthetic films protein based films have two major drawbacks [10–13]:

(i) poor mechanical properties (lower tensile strength and elongation at break);
(ii) a high water sensitivity i.e. high water solubility and water vapour permeability.

The aim of the present work was focused both on the improvement of the mechanical properties as well as the water resistance of caseinate based films. The first part of this study dealt with the control of the mechanical properties through addition of plasticizers. A plasticizer is defined as a low volatile organic compound which causes a decrease in polymer glass transition temperature (T_g) and an increase of flexibility and extensibility [14]. By decreasing intermolecular forces between polymer coils, the plasticizers cause an increase in material flexibility and conversely a decrease in the barrier properties due to the augmentation of the free volume [14,15]. To summarize, an initially hard and brittle material becomes soft and flexible when plasticized enough. Plasticizer efficiency is then mostly governed by its molecular weight and polarity. The most compatible plasticizers are also generally the most efficient. Polyols are often cited as good plasticizers for protein based materials [16–19] due to their ability to reduce intermolecular hydrogen bonding while increasing intermolecular spacing. Then, the mechanical properties of caseinate films were studied versus plasticizer type and content in the film. Since water behaves as a plasticizer [20], the plasticizing effect of polyol compounds was accounted for different relative humidity conditions.

In addition, caseinate based films were crosslinked with formaldehyde in the second part of this study. The occurrence of covalent bridges between protein chains allows water-insoluble three-dimensional network to be achieved. Crosslinking was combined to plasticizing for the achievement of caseinate films with improved mechanical properties and water resistance able to replace synthetic films and overcoming protein film drawbacks.

2. Experimental

2.1. Materials and reagents

Sodium caseinate (NaCAS) was purchased from Eurial (France). Its composition according to manufacturer data was: proteins 90.2%, water 5.7%, minerals 3.5%, fat <1%. Polyol type plasticizers including glycerol (Gly), triethanolamine (TEA), ethylene glycol (EG), di-, tri- and tetra-ethylene glycol (DEG, TEG, TeEG, respectively) were of analytical grade (purity 99+%, Acros Organics). Trinitrobenzene sulfonic acid was of analytical grade (Sigma). All other reagents, including potassium chloride (99+%), lithium chloride (99+%), magnesium nitrate (99+%), sodium azide (99%), sodium bicarbonate (99%) and formaldehyde (HCHO, 37 wt% solution in water stabilized with 10–15% methanol) were obtained from Acros Organics was used as received.

2.2. Film preparation

Aqueous mixture of protein (5% w/v) and plasticizer (plasticizer/protein ratios = 25%, 50% and 100% w/w, respectively) was magnetically stirred at 800 rpm for ~12 h at room temperature in order to get a homogeneous solution. Caseinate films were then obtained by the casting method: the film forming solution was spread onto a polystyrene plate and after the excess water was evaporated the film was peeled off. To study the role of relative humidity (RH) on mechanical properties, samples were kept in a closed tank containing saturated solutions of different salts for 7 days at 20 ± 2 °C. Three different RH were used: 11%, 53% and 84% with saturated solutions of KCl, $Mg(NO_3)_2$ and LiCl, respectively.

2.3. Chemical treatment

2.3.1. Crosslinking of plasticized films

Protein modification was performed with increasing aliquots of formaldehyde (37% w/v in water) in solution of sodium caseinate (5% w/w) in 4% $NaHCO_3$ buffer solution (pH = 8.6). For TEA plasticized samples, pH was controlled by TEA to 8.6 without the use of any buffer. The reaction with formaldehyde was performed with HCHO/NaCAS w/w ratios of 1%, 2%, 5% and 10%, respectively, corresponding to HCHO/Lys molar ratios of 0.67, 1.35, 3.37 and 6.75. Molar ratios were calculated in consideration of the 12.4 mol of potentially reactive amino acid residue, i.e. lysine (Lys), contained in 1 mol of NaCAS [21]. The ε-amino group of lysine