Mechanical properties and permeability of whey protein films

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ABSTRACT

Films of pure β-lactoglobulin, formed through the gel state, were studied in respect to mechanical properties in tension and oxygen transmission. The network structure was changed by varying pH and different concentration of plasticizer was added. The amount of plasticizer effected both mechanical and barrier properties whereas the difference in network structure only effected the mechanical properties.

INTRODUCTION

The increasing amount of waste is today a problem for the community. A major part of the waste comes from packaging materials. As an example, in Sweden about 50% v/v of the household waste is related to packaging materials, and the situation is similar in the rest of Europe. The waste is to a great extent either put in landfills or is incinerated, even though source separation and composting helps decreasing the amount. It would be environmentally sound to increase the two latter especially for packaging materials. However, the wide variety of plastics on the market prevents source separation and the non-degradable character of plastics prevents composting even for composite packaging materials where the major part often consists of degradable paper or cardboard.

A solution for this would be to increase the use of biodegradable materials. Degradable biopolymer films are both compostable and facilitate recycling of composite packaging materials. Environmentally it is even better if the biopolymer is produced from a renewable resource since that would not increase the CO_2 content of the atmosphere.

Whey protein films fulfil these environmental requirements and have also been shown to have good mechanical and permeability properties[1,2]. Whey is also fairly inexpensive compared to other biopolymers and has therefore a potential for being used commercially.

The dominant component of whey is β-lactoglobulin, both by amount and by influence on physical properties. The effects on the physical properties of β-lactoglobulin by pH have earlier been shown to be drastic[3]. Gels of β-lactoglobulin are fragile and transparent at low pH (<pH 4), more resilient but opaque at intermediate pH (pH 4-6), and rubber-like and transparent at high pH (pH >6). The properties and appearance of the gels depend on the microstructure of the network which is fine-stranded at low and high pH whereas it is particulate at intermediate pH.

Biopolymers generally form fragile films and plasticizers are therefore added to make the films more flexible[2]. An addition of glycerol or sorbitol has been shown to give the desired flexibility for whey films but also to increase oxygen permeability[1].

We have in this study used films of pure β-lactoglobulin at low and high pH to study the effect of network structure on mechanical and barrier properties of the films. The composition of the films were kept the same but the films had different types of fine-stranded networks. We also varied the amount of plasticizer.

MATERIAL AND METHODS

Material

The ß-lactoglobulin was produced at Laiterie Triballat, Noyal-sur-Vilaine, France after an industrial-scale fractionation process developed at Institut National de Recherche Agronomique (INRA), Rennes, France[4].

Sample preparation

The ß-lactoglobulin was dissolved in distilled water at 10% w/w and pH was adjusted with 0.1 M HCL or 0.1 M KOH to pH 3.0 or 7.5. Glycerol was added as plasticizer to 2 or 5% w/w. A glycerol content of 2% will be referred to as **low** and 5% as **high**. The samples were then degassed, heated to just below the gelation temperature and then directly poured into 11 cm Ø dishes. The solution was cooled and dried over night at 23°C in 50% RH. The dried films had a final thickness of 100-160 µm.

Methods

The tensile properties were studied using an Instron 1122 in accordance with ASTM D882-88. Rectangular strips of the films were cut and clamped between pneumatic grips. Force and elongation were recorded during extension up to **fracture** and stress and strain were calculated.

The small deformation properties was tested by Dynamical Mechanical Analysis (DMA) using an Rheometrics RSA II. A rectangular film strip was clamped in the instrument and a sinusoidal, **non-destructive deformation** was applied. The force and phase shift δ was recorded and the complex tensile modulus E^* was calculated. E^* can be divided into the storage modulus E' and loss modulus E" using the relations $E^*=E'+jE"$, $\tan \delta=E"/E'$, $j^2=-1$.

The ability of the films to act as **oxygen barriers** were measured in accordance with ASTM D3985-81 using Mocon Oxtran 2/90 equipment.

RESULTS AND DISCUSSION

Mechanical properties

The large deformation properties in Fig. 1 show clearly the effect of both microstructure and plasticizer content. The microstructure effects the mechanical properties in a similar way as for β-lactoglobulin gels[3,5]. The network of the films at pH 3.0 consists of straight, stiff strands and the films are fragile with low strain at fracture and no yield. At pH 7.5 the strands are longer and more flexible and so are the films. They have a pronounced yield and behave similar to synthetic films but with lower Young's modulus and lower fracture stress and strain.

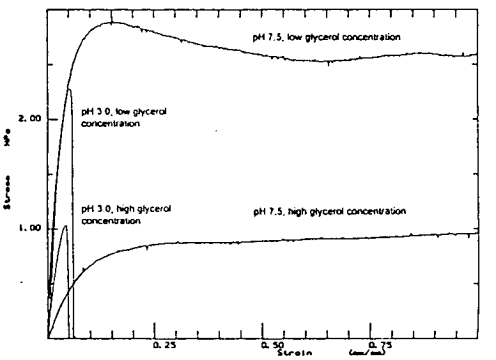

Figure 1. Stress-strain behaviour for ß-lactoglobulin films with varying microstructure and plasticizer content.

The addition of plasticizer has the same effect as published for whey films giving more flexible films with lower Young's modulus and lower fracture stress for both types of network structure.

At small, non-destructive deformations the amount of plasticizer has greater effect on pH 7.5 than at pH 3.0, see Fig. 2. The amount of plasticizer has almost no effect on the films at pH 3.0 indicating that the structure of the strands is not greatly effected. The phase angle is similar for all

samples, around 10°, except for pH 7.5 with high amount of plasticizer. The latter sample contains most water and has consequently a higher phase angle.

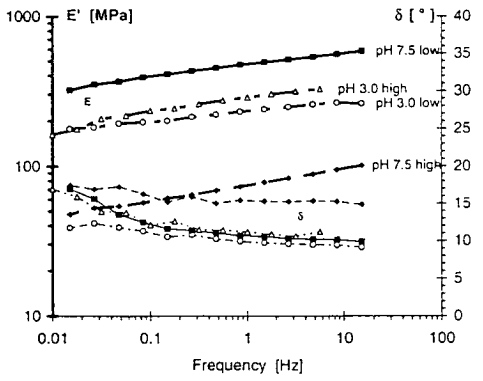

Figure 2. Storage modulus and phase angle of ß-lactoglobulin films by DMA.

Barrier properties

The oxygen transmission through the films is shown in Fig. 3. The network structure had no effect on the oxygen transmission, irrespective of plasticizer amount.

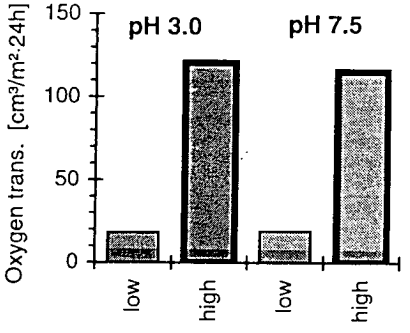

Figure 3. Oxygen transmission through ß-lactoglobulin films.

This may be explained by the gas diffusing through the pores of the film network and not interacting with the network strands. The composition of the films is the same leading to a constant transmission even though the network structure varies.

The oxygen transmission is low, even compared to good plastic films. Corresponding polypropylene films have as comparison 150 cm^2/m^2·24h.

CONCLUSIONS

- The network structure drastically influenced the mechanical properties of β-lactoglobulin films, both the fracture properties and small-deformation behaviour.
- A change in network structure had no effect on the oxygen transmission whereas an increased plasticiser concentration greatly increased the transmission.

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