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**PREPARATION OF FILMS FROM ISOLATE SUNFLOWER
(HELIANTUS ANNUUS) PROTEINS**

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ABSTRACT

The film-forming potential of isolate of sunflower proteins (ISFP) was investigated. Homogeneous films were obtained by dissolution of ISFP in alkaline water (pH = 12), addition of a plasticizer, casting and drying. The effects of five plasticizers (glycerol, 1,3-propanediol, D-sorbitol, triethylenglycol and tetraethylenglycol) on mechanical properties were studied.

Plasticizers conferred diverse tensile properties to the films : the use of 1,3-propanediol resulted in the highest tensile strength σ_{\max} (27.1 Mpa) and glycerol resulted in the greatest elongation at break ϵ_{\max} (251 %). Different mechanical properties were obtained by using mixtures of these plasticizers.

INTRODUCTION

In recent years, environmental concerns have increased the interest in biodegradable packaging materials. These materials are often formulated with biopolymers of agricultural origin capable to form a cohesive and continuous matrix.

Some plant proteins show properties that are advantageous in the preparation of packaging biomaterials, e.g., ability to form networks, plasticity and elasticity. Investigations on the film-forming potential of different plant proteins has mainly focused on soy proteins (Brandenburg et al., 1993), wheat gluten (Gontard and Guilbert, 1994), cottonseed protein (Marquie et al., 1995), and proteins extracted from sorghum kafirin, rice bran, peanuts, corn zein, and peas (Guilbert et al., 1997 ; Cuq et al., 1998).

Sunflower's oil cake obtained from the oil industry is an inexpensive source of proteins (more than 30 % content) that has been used mostly for animal feed purposes. It has been recently demonstrated that such proteins can be alkali-extracted to yield an isolate composed mainly of globulin and albumin (Leyris, 1998). It was therefore the objective of the present work to study the film-forming potential of sunflower protein isolate in order to propose an added-value outlet for the sunflower's oil cake and to contribute to the development of biodegradable packaging materials.

EXPERIMENTAL PROCEDURES

Film formation. Isolate of sunflower proteins (ISFP) (2g) was dispersed in 20 ml of distilled water. Alkalinity was adjusted to pH 12 with solid NaOH. The dispersions were stirred with a homogenizer (Ultra-turrax T-25, IKA, distributed by Aldrich, St. Quentin Fallavier, France) at 19 000 rmp for 14 min. After addition of a plasticizer (0.0109 mol), the mixture was stirred again (19 000 rpm, 1 min), then centrifuged (5 000 rpm, 5 min) to remove air bubbles and to separate the insoluble particles.

Solutions were cast in flat polystyrene petri boxes (Poly Labo, Strasbourg, France) measuring 12 x 12 cm, laying on a horizontal surface to maintain constant area and uniform thickness (170-200 μm). Films were allowed to dry for 24 h at $25 \pm 2^\circ\text{C}$, then peeled off from the plates and conditioned before testing.

Dumbbell-shaped specimens having standardized dimensions (75 x 5.5 mm, ISO 527-2, type 1BA), were cut off from the films. Thickness was measured to the nearest 0.01 mm with a hand-held micrometer (Braive Instruments, Checy, France). The average thickness was calculated from ten random measurements.

Plasticizer Content. The residual amount of plasticizer in films was determined by the meaning of the precise measurements of loss dry matter (gravimetric method) during drying of films at room temperature ($25 \pm 2^\circ\text{C}$). The observed difference was attributed to loose in plasticizer. This assumption was successfully verified by HPLC according to the method of Sanchez et al. (1998).

Films Conditioning. Before mechanical evaluations, film specimens were conditioned at 25°C and 60 % relative humidity for 24 h according to the European NF EN ISO 291 standard.

Tensile Properties. The mechanical properties were evaluated in a texture analyzer TA-XT2 (RHEO Stable Micro Systems, London, England). Five specimens were used for each film. Stress-strain measurements were used to determine the tensile strength (σ_{\max}) and elongation at break (ϵ_{\max}) values. The initial grip separation was 55 mm, and separation speed was 1 mm/sec, according to standards ISO 527-1 and ISO 527-2.

RESULTS AND DISCUSSION

Film Formation. The optimal solubilization of ISFP occurs at pH 12 (Leyris, 1998). This value was used to prepare the film-forming solution and NaOH was utilized to adjust the pH.

The films directly cast from the mother solution were too brittle to be handled. The addition of a plasticizer was therefore indispensable to obtain a flexible film. The plasticizer/ISFP ratio was decided in base of preliminary experiments that were carried out to determine the feasibility range of the films. Results using glycerol as plasticizer set the pattern for other plasticizers. We therefore decided to retain a glycerol/ISFP ratio of 1/2.

Effect of plasticizer. The protein-protein interactions, which determine the properties of the film, can be varied by the presence of a plasticizer. The lubricity theory of the plasticization mechanism accounts for this fact : the plasticizer acts as a lubricant to facilitate the movements of the protein chains over each other avoiding thus brittleness. In the previous experiments, the plasticizer used was glycerol (0.50 g/g ISFP). We investigated the effect of other plasticizers of polyol type on mechanical properties of films. All the plasticizers were added to ISFP in the same molar basis (0.00545 mol/g ISFP). After removal of the insoluble proteins, the plasticizer content in the film-forming solution was controlled again as described in the experimental section. It was verified that films contained comparable amounts of proteins (weight basis) and residual plasticizer (molar basis). The eventual lose of plasticizer in films during the drying step (25°C) was also controlled. As shown in table 1, the loss of plasticizer can be considered as negligible. It is therefore possible to compare the mechanical properties of these films.

The tensile strenght and the elongation of films cast with different plasticizers are shown in figure 1. The σ_{\max} -values varied between 1.8 and 27.1 Mpa and the ϵ_{\max} -values ranged between 1.6 and 251 %. Films cast with 1,3-propanediol presented the highest σ_{\max} , which is at least 14 times that of the film cast with TEEG (the smallest value). The σ_{\max} values of the other plasticizers : glycerol, D-sorbitol and TEG were comparable between them.

Plasticizers	Protein content (dry basis) (g)	Plasticizer content before film drying (mmol)	Residual plasticizer (mmol)	Lose of plasticizer over film drying at $\pm 25^{\circ}\text{C}$ (%)
Glycerol	1.671 ± 0.003	9.9 ± 0.4	9.7 ± 0.1	2.2 ± 0.3
1,3-Propanediol	1.669 ± 0.004	9.7 ± 0.5	9.2 ± 0.4	5.5 ± 0.2
D-Sorbitol	1.662 ± 0.005	10.0 ± 0.2	9.4 ± 0.3	6.5 ± 0.1
Triethylenglycol (TEG)	1.662 ± 0.005	9.9 ± 0.3	9.5 ± 0.2	4.9 ± 0.3
Tetraethylenglycol (TEEG)	1.667 ± 0.004	10.0 ± 0.4	9.4 ± 0.2	6.4 ± 0.1

Table 1. Water-ISFP films interaction for different plasticizers. Average and standard deviation values of 6 experiments.

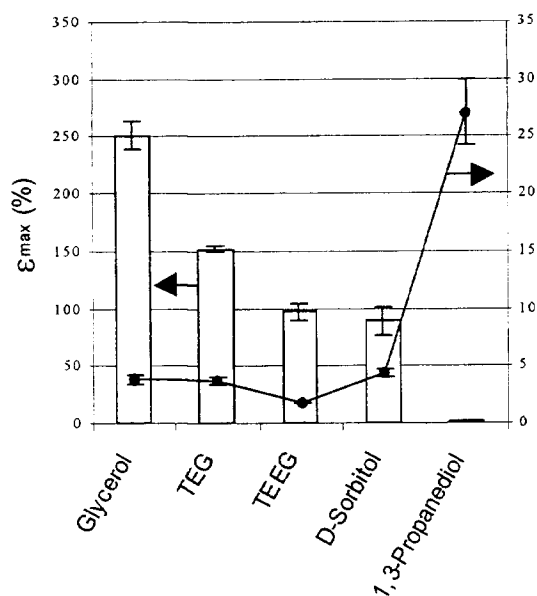


Figure 1. Effect of the plasticizer type on tensile strength (σ_{\max}) and elongation at break (ϵ_{\max}) of ISFP films. Plasticizer/ISFP = 0.00545 mol/g. Average and standard deviation values of 5 experiments.

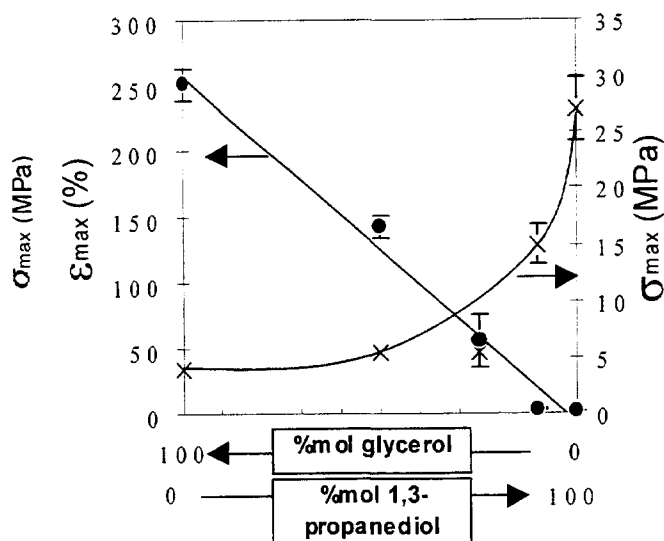


Figure 2. Mechanical properties of ISFP films cast with mixtures of glycerol and 1,3-propanediol. Total plasticizer/ISFP = 0.00545 mol/g. Average and standard deviation values of 5 experiments.

In the case of glycerol, ISFP films were more elastic and resistant ($\sigma_{\max} = 3.9$ Mpa and $\epsilon_{\max} = 251$ %) than films obtained from isolate of soy proteins (3.3 Mpa and 100 % ; Krochta, 1997) at comparable content of plasticizer [37 % w/w vs. 35 % (dry basis) in our case].

It was observed that 1,3-propanediol yielded the film with the highest tensile strength but with the poorest elasticity. Conversely, glycerol conferred the highest elasticity associated to moderate strength. It was therefore interesting to perform combinations of these two plasticizers, in different percentage blends, to seek a compromise between tensile strength and elasticity (figure 2).

When increasing from 0 to 75 % the percentage of 1,3-propanediol in the mixture of plasticizers, the σ_{\max} -values increased only slightly, but in the range 75-100 %, the total increase was remarkable (about 600 %). On the other hand, ϵ_{\max} -values decreased linearly in the whole range. In an equimolar mixture, an increase of about 40 % in tensile strength ($\sigma_{\max} = 5.5$ Mpa) was obtained with a loss of about half of the elasticity ($\epsilon_{\max} = 142$ %).

CONCLUSION

This study demonstrates that it is possible to prepare films from sunflower proteins by an alkaline casting process.

The drying of films at room temperature permitted to obtain comparable amounts of residual plasticizer on the films formed. Plasticizers conferred diverse tensile properties to the films : the use of 1,3-propanediol resulted in the highest σ_{\max} and glycerol resulted in the greatest ϵ_{\max} . Mixtures of these plasticizers do not improve both mechanical properties at the same time. Nevertheless, different mechanical properties were obtained by this means. These results open new outlets for the exploitation of sunflower residues.

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