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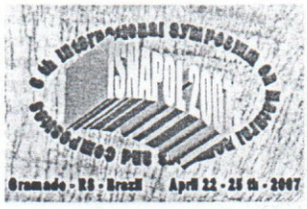
SURFACE WETTING AND DMA CHARACTERIZATION OF ZEIN/OLEIC ACID BASED FILMS



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The objective of this study was to evaluate the effect of oleic acid (OA) addition as plasticizer on mechanical and wetting properties of zein thin-films. The films, typically hydrophobic, were obtained by casting from ethanol solutions with different concentration of OA, and water contact angle and tensile properties characterized. No significant effect was observed in the surface wetting value on the films independent of the composition. All samples presented similar contact angle (around 68°) with a general trend to a receding drop along the time. Evaluations of mechanical properties by DMA (Dynamic Mechanical Analysis) showed an enhancement of tensile strength and elongation with the presence of plasticizer. 1% wt of OA showed to has a good effect on mechanical properties for long term film storage.

Introduction

Zein is the main storage protein in the corn endosperm and makes up more than half the total mass of the seed proteins. Zein offers a range of products for agricultural, food, pharmaceutical and industrial applications (1-3).

Actually, zein comprises a mixture of proteins classified according to their solubility and molecular rates as three different polypeptides: α, β and γ zeins. α-Zeins are the most abundant, with 75 to 85% of the total maize proteins, and characterized as alcohol-soluble. Since zeins are natural and biodegradable polymers obtained from renewable resource, an increasing interest has seen recently, in particular due to the potential for uses of this material as substitute for synthetic plastics.

The zein proteins display significant hydrophobic properties with ability to form edible films, suitable for applications as gas and moisture-barrier, for food and drugs coatings and protection (4).

Traditionally, films made from commercial zein are too brittle and their tensile strength too low that limits a broad range of uses. To overcome such disadvantage, low molecular-weight plasticizers (for example, glycerol and lipids) are necessary to be added to protein films in order to improve film flexibility by reducing the chain-to-chain interactions.

The addition of plasticizer introduces not only mechanical changes but also the surface charges are presumably affected as function of a structural reconformation of proteins in the presence of such substances. Since hydrophobicity is related to wetting, which involves the interaction of a liquid (usually water) to the surface, the change on charges alters the film surface's wettability.

In this work mechanical properties (evaluated by DMA analysis) and surface's wettability (evaluated by water contact angle) of zein films prepared with different percentage of oleic acid (OA) as plasticizer are characterized.

Experimental

Zeins extraction and film processing

Zeins were extracted from corn gluten meal (CGM), gentility supplied by Corn Products Inc. CGM is a by-product of starch production in the wet-milling process. This product has up to 70% zeins and some residual polysaccharides not removed in the process (5,6). Initially the CGM was treated with hexane in soxlhet apparatus (along 24 h) to remove the oil fraction of CGM. The residual mass was mixed with 70% ethanol during 24 h. The zein proteins were obtained by solvent evaporation and then lyophilized (6).

Zeins solutions were prepared using 70% ethanol as solvent in a concentration of 4.2% in mass. The oleic acid (OA) were separately added in the proportion of 0.25; 0.50 and 1.0% wt. Films were prepared by solution casting onto an acrylic plate. Solvents were allowed to evaporate at room temperature. After drying the films were peeled from the plate.

Wetting and mechanical properties

Contact angles were determined by the visual angle measurement at room temperature using a 50μL drop of deionized water. The contact angle was dynamically

recorded using a video-based device and the angles were digitally determined by FTA32 Image Software (First Ten Ångstroms). The average of five measurements was considered in each sample. All measurements were performed under air atmosphere at room temperature.

Dynamic mechanical analysis (DMA) was performed in all samples (thickness $\theta \cong 50$ μm), using a TA Instrument DMA 2930, in tensile mode. The elastic damping coefficient was function of temperature, for a frequency of 1 Hz, heating rate of 5°C mim^{-1} and amplitude of 20μm.

Results and Discussion

The measured contact angle on films with different OA concentration was not statistically significant. The initial contact angle values ranged around 68° on all samples, with a small standard deviation (± 3). However, it was possible to observe a time-dependence behavior, with receding angle, mainly in the first 5 minutes, as seen in Figure 1.

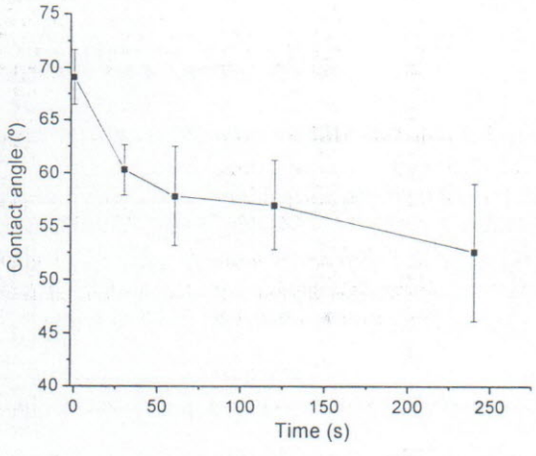

Figure 1 – Example of contact angle versus time as measured. Receding angle on film with 1% wt of OA.

This receding behavior could be interpreted as an indicative of absorption capacity or water being trapped due capillary forces in the film-water interface. In this regard, a zein's tendency of a hydrophilic character is observed instead of hydrophobic. According to Muthuselvi and Dhathathreyan (7), such behavior is understood due to the presence of plasticizer molecules in the polymeric chains, which provoke a reorientation of the polar groups towards the interface and also a reduction on the number of aminoacid residues exposed to the solvent.

The contact angle is dependent on the liquid surface tension and in general decreases as the surface tension decreases. In other words, the presence of plasticizer makes the zein less water repellent. Besides, the contact angle values measured on our samples are in good agreement with that found in the literature for zeins films plasticized with glycerol and sorbitol (7).

The mechanical properties, analyzed by DMA technique, showed significant differences amongst zein mixed with plasticizer. In general, all films exhibited brittle failure with little plastic deformation (maximum 2%) and moderately resistent. However, films prepared with different plasticizer concentration exhibited variations in their resistance to breakage; i.e., higher plasticity is attained as the AO proportion increases. Figure 2 presents the effect of OA concentration on the mechanical properties of zein films. After two months stored to the room conditions (Figure 3) it was observed an increasing in elasticity and rupture resistance. This behavior was pronounced in films containing 0.25 and 0.5% of OA. This effect is not fully comprehended, but it is important to notice the great influence of storage time on the mechanical properties.

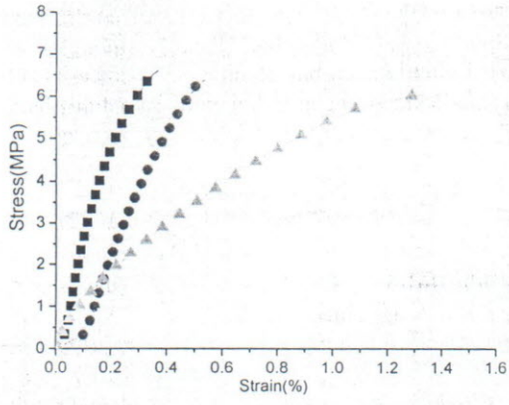

Figure 2 - Stress-strain curves for zein films recently prepared with different content of oleic acid: 0.25 % (■); 0.50% (●) and 1.00% (▲) at room temperature.

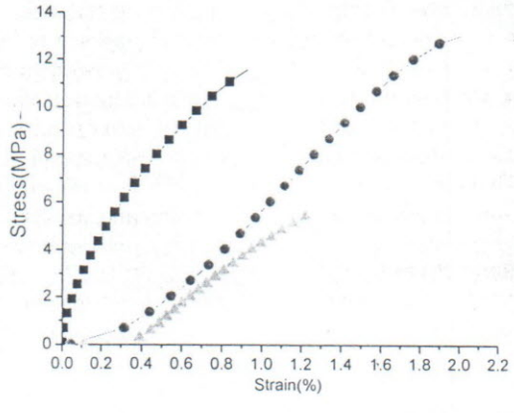

Figure 3 - Stress-strain curves for zein films after 2 month of storage with different content of oleic acid: 0.25 % (■); 0.50% (●) and 1.00% (▲) at room temperature.

Conclusions

Concerning the wettability of zein films, our results indicate that films processed with CGM extracted zeins, using OA as plasticizer, behave similarly as zein

films commercially obtained and plasticized with glycerol and sorbitol.

It is observed a hydrophilic wetting effect although zeins are very hydrophobic proteins. Such characteristic was assumed as a result of the reorientation took place on the surface due the action of the water. Also the plasticizer presence can promote a restructure over the chains as consequent of the decreasing on the hydrofobic aminoacid residues exposed to the solvent.

The DMA clearly demonstrates the benefit of using oleic acid as plasticizer in the processing of zein films. In general, the plasticizer improved flexibility of films, which prevents cracking or chipping of films during their preparation, handling and storage.

Aknowledgements

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References

1. J.A, Rothfus. *J. Agric. Food Chem.* 1996, *44*, 3143-3152.
2. R, Lasztity. *The Chemistry of Cereal Proteins* CRC Press, New York, 1996.
3. L.A. Forato, V.E.Yushmanov, L.A. Colnago, Biochemistry, 2004, 43, 7121-7126.
4. L.M. Covre, O.B.G. Assis, P.B.T. Piza, L.A. Colnago, L.A. Forato. *In:* Proceedings of International Macadamia Symposium, São Pedro, Brazil, 2006, 93-96.
5. S.Wu, D.J. Myers, L.A. Johnson, *Cereal Chem* 1997, 74, 258-263.
6. L.A. Forato, T.C. Bicudo, L.A. Colnago *Biopolymers (Biospectroscopy)* 2003, 72, 421-426.
7. L Muthuselvi, A Dhathathreyan, Pramana, J. of Physics, 2006, 66(3), 563-574.