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## MECHANICAL TESTING OF CHITOSAN AND ZEIN THIN FILMS FOR PACKAGING PURPOSE

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**ABSTRACT:** The objective of this study was to compare the mechanical properties of hydrophilic chitosan thin films to hydrophobic zein films with different additions of oleic acid (OA) as plasticizer. The films were obtained by casting from precursor solutions (chitosan acid solution and zein alcohol formulation) on room temperature. The mechanical properties were evaluated by DMA (Dynamic Mechanical Analysis) showing the importance of using plasticizer in enhancing the protein tensile strength and elongation. The results were compared to conventional packaging materials as commercial PVC films and soft bleached wrapping paper.

**KEYWORDS:** chitosan, zein, natural polymeric films, packaging materials.

**INTRODUCTION:** Chitosan is a biocompatible, biodegradable and non-toxic linear polymer, commercially available by the deacetylation of chitin, an abundant polysaccharide extracted from the shells of shrimps and crabs. One function of particular interest is their broad antimicrobial activity (SUDARSHAN et al., 1992) in conjunction with their excellent film forming ability (KITUR et al., 1998) with no necessity of plasticizer additions (BRITTO et al., 2005). Moreover, the biocompatibility and the biodegradability of chitosans make them a very interesting polymer for applications in food, such as in packaging or edible coatings to extend shelf-life and preserve quality of fruits and vegetables (ASSIS & PESSOA, 2004; ASSIS & HOTCHKISS, 2007). Since chitosan is a hydrophilic polysaccharide, the plasticity of chitosan films has been attributed to the effect of inter-chain water (BRITTO et al., 2005). On the other hand, zein is a hydrophobic material, being the main constituent of the storage proteins in the corn endosperm and makes up more than half the total mass of the seed proteins. Zein also has good film forming ability, being suitable for applications as gas and moisture-barrier and effective action on decreasing bacterial population when used as edible coating (CARLIN, et al., 2001), offering a range of products for agricultural, food, pharmaceutical and industrial applications (ROTHFUS, 1996).

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.

In this work mechanical properties (evaluated by DMA analysis) of commercial medium molar chitosan and zein films (extracted from gluten), prepared with oleic acid (OA) as plasticizer, are characterized and compared to conventional packaging materials as commercial PVC films and soft bleached wrapping paper.

**METHODOLOGY:**

Commercial-grade chitosan was purchased from Polymar (Brazil). Aqueous acetic acid solution (1%) was used to prepare chitosan precursor solution. Zein was 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% of zein's type proteins and some residual polysaccharides not removed in the process (FORATO et al., 2003). Initially the CGM was treated with hexane in soxhlet 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. Zein solutions were prepared using 70% ethanol as solvent in a concentration of 4.0% 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 acrylic Petri dishes at room temperature. After drying the films were peeled from the dishes (thickness  $\theta \cong 50 \mu\text{m}$ ). DMA analysis (TA Instrument DMA 2930, tensile mode, heating rate:  $5^\circ\text{C} \text{mim}^{-1}$ , amplitude:  $20\mu\text{m}$  and frequency: 1 Hz). Commercial PVC films (WydaPratic, 0.050 mm thickness) and soft bleached wrapping paper (0.010 mm) were also tested for comparison.

**RESULTS AND DISCUSSION:**

By dynamic mechanical analysis (DMA), the chitosan films revealed non-linear viscoelastic behavior, exhibiting a stress vs. strain curve typical of brittle material (Figure 1) which is characterized by a decrease in the percentage of elongation at break. Such materials do not present a Hookian behavior (elastic or reversible deformation zone) but only a plastic or irreversible deformation zone. As consequence, they do not yield the limit point of elastic deformation stress. The chitosan films exhibited very small plasticity (Table 1), nevertheless revealed sufficient mechanical strength when assessed in terms of the force of and percentage elongation. They showed no signs of breaking down in the range of the applied force (0-15N). The literature reports tensile strength ranging from 50 to 150 MPa corresponding to deformation in the order of 8% to 40% (RATHKE et al., 1994). In this way, several factors affect the interchain interactions and the chitosan dynamic rheology during stretching, such as molecular weight, degree of deacetylation, water content and crystallinity of the polymer. The values of Young's modulus for chitosan are in good agreement with those reported in the literature (BÉGIN & CALSTEREN, 1999).

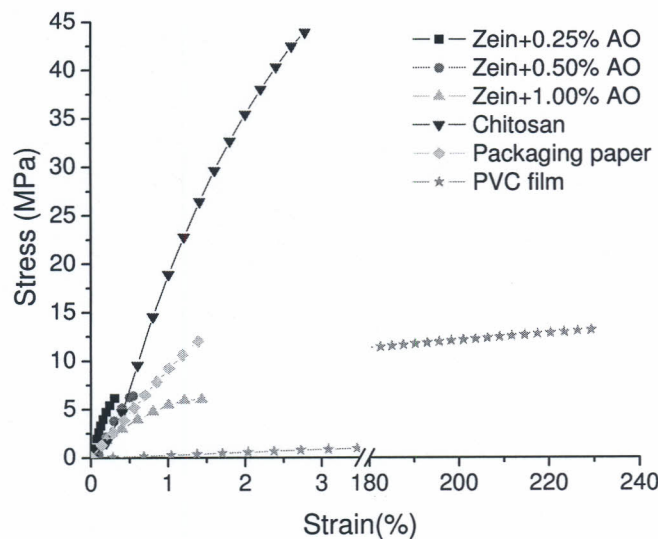


Figure 1. Stress-strain curves for chitosan and zein films at room temperature

The mechanical properties of zein films showed significant differences amongst zein mixed with plasticizer. In general, all films exhibited brittle failure with little plastic deformation (maximum 2%) and moderately resistant. 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 as shown in Table 1 where the maximum strain values increase and Young's modulus decrease as AO proportion increases.

By comparing zein and chitosan films with wrapping paper and PVC film (Figure 1) it can be observed that mechanical behavior of the zein films are close to the paper's, though the protein films are quite brittle, tearing at low applied strain. Amongst the natural tested materials, the chitosan presented better performance with a relatively higher plasticity and rupture resistance. Nevertheless, all materials are considerably inferior to mechanical features of PVC films, which maximum strains are close to 230% (Table 1).

TABLE 1. Values of Young's modulus (MPa) and maximum strain (%) for the tested materials.

Sample	Young's modulus	Tensile strength	Maximum strain
Chitosan	2283	> 44.0	2.8
Zein (0.25% OA)	2309	6.6	0.4
Zein (0.50% OA)	1587	6.4	0.5
Zein (1.0% OA)	418	6.0	1.4
Soft Packing Paper	768	12.4	1.9
PVC film	4.2	13.2	230

The zein films had low oxygen, carbon dioxide and water vapor permeability, and therefore its potential as bio-based packaging technologies to improve the quality and safety of fresh and processed foods. The tensile strengths of the zein films are in good agreement with the literature and in work conducted by YOSHINO, et al., 2002, it was pointed that the mechanical properties of the zein films showed to be depended on the drying conditions during preparation. The differences in physical properties of the different zein films were most likely caused by variation in the internal microstructure of the zein films.

Anyway, in spite of its fragility, renewable and environmental friendly materials such as zein and chitosan films have potential to be an alternative to petroleum-based packaging materials. They also are contemplating incorporating antimicrobial agents into the films that would then be applied to food products or packaging materials to inhibit microbial growth. Both materials are already used as modified atmosphere coating for shelf-life extension and are possible substitute for polyolefin films, deserving intensive studies. By changing plasticizer and film preparation procedures, we expect that it will be possible to make chitosan and zein films with various useful physical properties.

**CONCLUSION:** Films chitosan are more plastic than zein, although all casted films demonstrated brittle material characteristics. The analysis showed that films with different characteristics of elongation and hardness can easily obtained by means of combined of zein an oleic acid. For these, the best properties were attained for the combination of zein (4.2%) with 1% of plasticizer. For these the mechanical behavior was close to soft bleached paper. Chitosan presented better mechanical features although all materials are quite inferior to synthetic PVC films.

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