

Mechanical Analysis of Biodegradable Films from Native and Chemically Modified Potato Starches

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Abstract. The production of biodegradable films has been studied to be a substitute of conventional plastics. The use of starch in biodegradable films are of great interest and starch modification improves an increase to the mechanical properties the film. The mechanical properties were evaluated by Dynamic Mechanical Analysis (DMA). The aim of this study is to determine the mechanical properties of biodegradable films produced from native and chemically modified potato starch. The starch was extracted and subjected to chemical modification by oxidation in different concentrations of active chlorine. The biodegradable films were prepared with starch and glycerol as plasticizer, and were observed with an optical microscope to evaluate the morphology and their relationship with the strength. The tensile tests were performed at 80°C to evaluate the mechanical properties by means of stress-strain curves. The morphology of biodegradable potato starch films shows that the starch granules were partially gelatinized during the film formation. As the elastic modulus is a property which determines the stiffness of the material, by means of he DMA analysis it can be seen that oxidation results in beneficial changes in the mechanical properties of the films, because the modulus increased from 346.70 MPa for the native starch to 651.75 MPa to oxidized starch with 1.5% of active chlorine, respectively.

Introduction

Biodegradable materials are being widely used as food packaging in order to ensure food security and safety, also to replace the conventional plastics because of the growing concern about the environmental impact. Despite its higher cost, compared to conventional plastics, companies are investing due to environmental awareness [1,2,3,4].

As the use of biodegradable films is increasing, one of the currently raw material used for its production is starch, since is readily available, versatile and because it is easily extractable [2,5]. Starch is a polysaccharide found in the form of granules stored in plants like tubers and cereals composing 65% to 95% of its dry weight [6,7]. The film is obtained by gelatinization of the starch in water in temperatures between 70°C to 90°C in the presence of a plasticizer in order to produce a durable thermoplastic starch. One of the most used plasticizers is glycerol that provides the final thermoplastic mechanical properties [8,9].

These starch-based films are colorless, environmentally friendly, flexible and non-toxic. Although the films from native starch do not have such good characteristics as conventional plastics and their application is limited. Thus, the starch may be chemically modified by oxidation, performed with controlled pH and temperature, which improves its value and use to produce resistant films with high quality, barrier and mechanical properties [10,11,12,13,14,15].

The mechanical properties depend on the formulation and preparation of the films. The mechanical behavior analysis of the films is useful because can be directly applied on the food packaging resistance. The results of this analysis can indicate the possibility to replace the conventional plastics by these kind of materials [16]. These properties are important to preserve the processing, storage and handling of the material, and are critical in its several applications. A technique that can be used for evaluation of the mechanical strength is Dynamic Mechanical Analysis (DMA) [17,18].

DMA is a rapid technique that requires small amounts of material. The viscoelastic materials, such as polymers, exhibit a deformation behavior that depends on the strength, temperature and frequency that was exposed. Through this behavior, it is possible to analyze several properties [19,20,21]. The mechanical test by DMA is used due to their high resolution of the deformation measurements, to obtain the elastic modulus, and depending on the performed test, the module may result as being tensile, flexural or compressive [20,21,22].

The aim of this study was to determine the mechanical properties of biodegradable films produced from native and chemically modified potato starches, with different concentrations of active chlorine, by DMA technique.

Materials and Methods

Starch isolation. The potatoes (*Solanum tuberosum L.*) were peeled and immersed in distilled water with sodium bisulfite 0.1% (1:7 w/v) for 2 hours. The dispersion was triturated in a blender, sieved, and decanted. The starch was washed at least three times using distilled water and dried in an oven with forced air circulation at 40 °C until a moisture content between 7% to 10% was reached.

Starch oxidation. The chemical modification of starch was performed by the oxidation method described by [23] with some modifications. The starch was suspended in distilled water heated to 40 °C and subjected to treatments with sodium hypochlorite in active chlorine different concentrations (0.5% and 1.5%). The pH was adjusted to 7.0 using 0.5M hydrochloric acid and 0.5M sodium hydroxide while the sodium hypochlorite was added slowly over a period of 1 hour of reaction. The starch was filtered through a medium porosity filter paper in a Buchner funnel, washed with 1200 mL of distilled water, resuspended in distilled water and filtered again three more times at room temperature. The oxidized starch was dried in an oven with forced air circulation at 40°C until a moisture content of between 7% to 10% was reached.

Films preparation. Starch-based film solutions were prepared by dissolving glycerol as plasticizer (concentration 0.30 g glycerol/g starch) in distilled water with 3.0% of starch in the suspension. The solution was heated to 90 °C under stirring for 5 minutes to promote the starch gelatinization. The film solution was added on acrylic plates for drying in an oven with forced air circulation at 40 °C.

Optical Microscopy. The biodegradable films were observed with an optical microscope. Micrographs of biodegradable films were taken for evaluation of its morphology and visual analysis.

Dynamic Mechanical Analysis (DMA). The analysis was performed on TA Instruments DMA Q800™ equipment. Tensile tests were performed in controlled force mode using a tension film clamp. In order to obtain the stress-strain curve, this test was performed at 80 °C and the ramp force initiated in 3 N/min until 18 N.

Results and discussion

Optical Microscopy.

The optical microscopy was used to observe the morphological structures of polymeric materials and the effects of treatments applied to these materials. Fig. 1 and Fig. 2 represent the micrographs of the biodegradable films of native and oxidized potato starches.

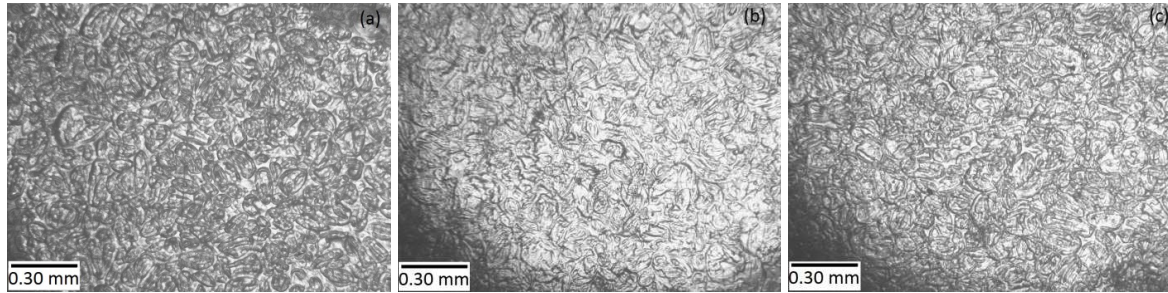


Fig. 1 –Micrographs of biodegradable films of (a) native potato starch, (b) oxidized potato starch with 0.5% of active chlorine and (c) oxidized with 1.5% of active chlorine.

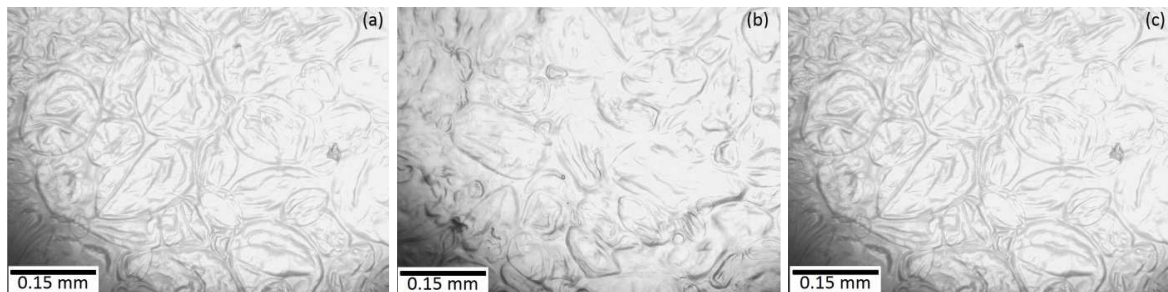


Fig. 2 –Micrographs of biodegradable films of (a) native potato starch, (b) oxidized potato starch with 0.5% of active chlorine and (c) oxidized with 1.5% of active chlorine.

During the heating of solution is leached amylose to intergranular space and the granules begin to break down occurring the breaking of the hydrogen bonds and solubilized amylose and amylopectin. After lowering the temperature of the solution, the retrogradation occurs and the amylose and amylopectin chains tend to move together by hydrogen bonding. It is possible to observe in the micrographs non-gelatinized starch granules. This can be because there was no complete rupture of hydrogen bonds between amylose and amylopectin. It results in partial gelatinization of granules [24,25,26,27].

Dynamic Mechanical Analysis (DMA).

Tensile tests were performed to obtain the stress-strain curves as it was shown in Fig. 3. The elastic modulus and the yield strength, calculated by ASTM E-111, and tension at break are exhibit in Table 1.

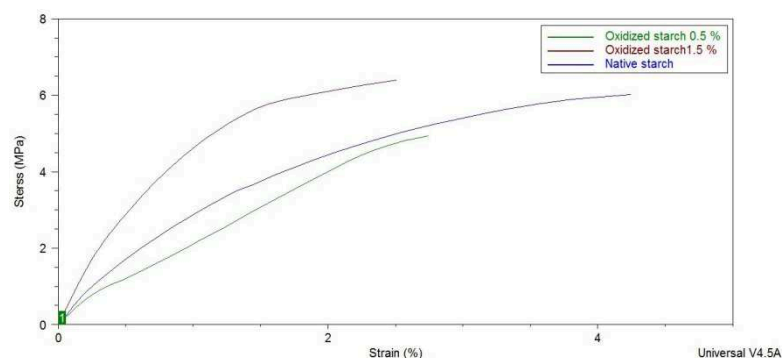


Fig. 3 –Typical curves of tensile test for biodegradable films of native potato starch, starches oxidized with 0.5% and oxidized with 1.5% of active chlorine.

Table 1 – Elastic modulus [MPa], Yield strength [MPa] and Tension at break [MPa] for biodegradable films of native potato starch, starches oxidized with 0.5% and oxidized with 1.5% of active chlorine.

Films ^a	Elastic modulus [MPa]	Yield strength [MPa]	Tension at break [MPa]
Native Starch	346.70	3.12	5.94
Oxidized Starch 0.5 %	229.65	1.84	4.44
Oxidized Starch 1.5 %	651.75	4.15	6.38

^a Starches oxidized with 0,5 % of active chlorine and 1,5% of active chlorine.

Dynamic mechanical analysis provides an accurate means of measuring the elastic modulus of films by tensile test. The film of oxidized potato starch with 0.5% of active chlorine showed a lower elastic modulus as compared with the film of native potato starch. However, this parameter increased because of the increasing in oxidation of starch to 1.5% of active chlorine. This shows that oxidation with the highest concentration of active chlorine improves the mechanical properties of the films.

According to ANOVA and t-student test, $p \leq 0.05$, the elastic modulus showed significant differences between the samples of native starch film and film of oxidized starch with 1.5% of active chlorine, as well as the film of oxidized starch with 0.5% when compared to 1.5% of active chlorine. However for the films of native starch and oxidized with 0.5% had no significant difference.

The yield strength and the tension at break had no significant difference between the samples according to ANOVA and t-student test, $p \leq 0.05$.

Conclusions

For micrographs of biodegradable potato starch films has been observed that the starch granules were not completely gelatinized in film formation.

The DMA measurements indicated that the oxidation of potato starch with a higher concentration of active chlorine improved the mechanical properties of the films, since increased the elastic modulus as compared to film of native starch.

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