Analysis of mechanical traction in biofilms chitosan and clay aiming fruits coating

Analise de tração mecânica em biofilms de quitosana argila visando revestimento de frutas

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ABSTRACT - A new concept of food packaging has been studied and developed in order to meet the application needs of the market. The application of such biofilms coating is directly related to its characteristics and possible interactions of these with the product and the environment. There is evidence that chitosan is a viable alternative to be applied in the coating for fruit characteristics antifungal, antibacterial and its direct action as a barrier to water vapor, which is the latest aging fruit. The clay, besides increasing permeability to water vapor, enables a greater adhesion of the film on the fruit surface. This paper presents the results that were obtained from the development of chitosan films aimed at applying the coating of fruit. It were made tensile tests with films using different chitosan and clay concentrations. The tests followed the standards of ASTM D882/02. The best results were obtained for the coating of chitosan in 2% acetic acid, which showed a plastic strain of 4.4% and a maximum stress at rupture of 50.2 MPa. The results were lower for the films with the addition of clay; the best result was observed for this coating with chitosan to 2% clay plus 2% acetic acid, with plastic deformation of 2.9% and maximum stress at rupture 18.9 MPa.

Keywords: biofilms, chitosan, clay, maximum stress at rupture, plastic deformation.

RESUMO - Um novo conceito de embalagem de produtos alimentares vem sendo estudado e desenvolvido no intuito de satisfazer as necessidades do mercado. A aplicação de filmes para revestimento está diretamente relacionada às suas características e possíveis interações destes com o produto e o meio ambiente. Há evidências de que a quitosana é uma alternativa viável no revestimento de frutas devido suas características antifúngica, antibacteriana e a sua ação direta como uma barreira ao vapor de água. A argila, além de aumentar a permeabilidade ao vapor de água, permite uma maior aderência do filme sobre a superfície do fruto. Nesse trabalho foram sintetizados filmes de quitosana e argila, em diferentes concentrações, e foram realizados ensaios de tração. Os testes seguiram as normas da ASTM D882/02. Os melhores resultados foram obtidos para o revestimento de quitosana em ácido acético a 2%, o que mostrou uma deformação plástica de 4,4% e uma tensão máxima na ruptura de 50,2 MPa. Os resultados foram inferiores para os filmes com adição de argila; o melhor resultado foi obtido para o revestimento com quitosana a 2% de argila mais ácido acético a 2%, com deformação plástica, de 2,9% e tensão máxima na ruptura de 18,9 MPa.

Palavras-chave: biofilmes, quitosana, argila, tensão máxima de ruptura, deformação plástica.
INTRODUCTION

The use of biodegradable materials as a possible solution to environmental problems has received much attention these days because the plastic packaging developed by industries are petroleum-based and short-term are not biodegradable (Sorrentino et al., 2007). Several studies have been conducted in recent years in order to develop and characterize biofilms with potential application mainly in the food and agriculture.

The polymers used for the production of biofilms is extracted or removed from the biomass (proteins and polysaccharides); produced by microorganisms (xanthan gum, etc.), or by chemical synthesis from monomer biological sources, or even by mixing sources Biomass and oil (or biopolymeric acid polyester) (Batista et al. 2,005; Yu et al. 2006).

Biofilms are prepared from biological materials which act as a barrier to external factors and, therefore, may protect the product and to increase its shelf life (Tanada-Palmu, et al. 2002), controlling moisture loss of gas exchange tissues of fruits and breathing, increased durability, functioning as an alternative treatment for controlled atmosphere (Avena-Custillos and Krochta, 1993).

Among these materials, chitosan has been used as an important material in science and industry for their unique properties, since it offers potential advantages as a raw material for the production of films, covers and plastic applications, in addition to being biodegradable and renewable (Rao et al. 2010). Chitosan is a biopolymer that can be used to form biodegradable films with a good efficiency in maintaining the microbiological quality of the food (Dotto, et al. 2008).

However, in general, biopolymers exhibit poor mechanical and barrier properties, which need to be improved so that they can be used in different applications. Polymers produced with the addition of nanoparticles often exhibit properties superior to conventional composites such as higher mechanical strength, better consistency, increased thermal and oxidative stability, better barrier properties to gases and water as well as flame retardamento (Sozer and Kokini 2009).

The bentonite clay is used in this study as a composite material of the biofilm. The clay obtained in the region of Seridó-RN-Brazil, at low cost, also allows a greater adherence of the biofilm on the surface of the fruit (Lavorgna, et al. 2010). These improved properties are generally achieved in the space filled by polymer matrix compared to conventional materials. With respect to biodegradability, these materials also have advantages (Pavlidou and Papaspyrides, 2008).

When used in fruit post-harvest use of these films causes changes in the physiology of fruit and therefore may interfere with the parameters of post-harvest quality.

Based on the above this work aims to synthesize biofilms chitosan / clay and analyze the mechanical properties of the films, for their application in coatings for fruits.

MATERIALS AND METHODS

Chitosan/Clay

The chitosan used in this study was obtained commercially. According chitosan is received form high density features aspect of yellowish powder and coloring in white. The bentonite clay is used in this study as a composite material of the biofilm. The clay obtained in the Seridó-RN-Brazil region.

Preparation of films

The solutions were prepared by dissolving moderate agitation in 0.5 M acetic acid until equilibrium with pH around 3 to chitosan solutions with concentrations of 1% and 2 as described by Assis et al (2002). This pH was adopted by theoretically be the maximum solubility of chitosan. Periods of up to 24 hours of shaking were required to obtain a complete homogenization of the solution with a magnetic stirrer. To simplify the entire procedure was performed under ambient temperature of approximately 29 ± 0.1 ° C.

For the formation of the film casting method was used which is deposited 5 mL of the chitosan gel in acrylic plates 10 x 10 cm and were left at room temperature until all the water was completely evaporated (temperature around 29 ± 0.1 ° C and time of about 72 h). After evaporation of all the water present in the gel, the film is formed and subjected to testing. The films will have their thicknesses controlled by fixing the quantity of raw dried (chitosan + clay) present in each plate.

The films were named with respect to the concentration of chitosan present in the matrix, 1, and 2% (10 and 20 g / L) by adding clay as follows: Q1 - Movie with chitosan concentration of 1%; Q2 - Movie with chitosan concentration of 2%; Q1A - Movie with chitosan concentration of 1% and 1% clay; Q2A - Movie with chitosan concentration of 2% and 2% clay.

Characterizations

The characterizations were: thickness, strength and maximum tensile plastic deformation. The thickness was determined with the aid of a manual micrometer. The thicknesses were performed on three of the films cut for mechanical testing, the result consisted of the average of points assessed, expressed in mm. Assays were performed in triplicate. The mechanical tests were performed on the equipment DL 10000/EMIC, according to the standards of ASTM D882/02. The films were cut forming strips of 100 mm by 20 mm and subjected to traction.

RESULTS AND DISCUSSION

Thickness

Table 1 shows the effect of the concentration of chitosan and clay in film thickness. In Table 1 it can be seen that the thicknesses of the films vary from 0.037 to 0.097 mm. The values approach the commercial film of polyethylene. The increase in chitosan concentration causes...
an increase in film thickness. It was also observed an increase in the thickness when the addition and no increase in the clay concentration, which occurs due to the increase of dry matter deposited. The thickness data are used to calculate the maximum tensile stress and plastic deformation. Tavares et al. (2010) shows thicknesses from 0.190 to 0.230 mm zein films with clay additives, where they are compared to a polyethylene film of 0.050 mm.

### Table 1 - Effect of chitosan and clay concentration in the thickness of the samples films.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>THICKNESS</th>
<th>UNIT</th>
</tr>
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<tbody>
<tr>
<td>Q1</td>
<td>0.037</td>
<td>mm</td>
</tr>
<tr>
<td>Q2</td>
<td>0.055</td>
<td>mm</td>
</tr>
<tr>
<td>Q1A</td>
<td>0.086</td>
<td>mm</td>
</tr>
<tr>
<td>Q2A</td>
<td>0.097</td>
<td>mm</td>
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#### Mechanical tests

The data were analyzed, and then built the Table 2 with the values of maximum voltage ($\delta_{\text{max}}$) and plastic deformation ($\xi$):

In Table 2 it is clear that increasing the concentration of chitosan increased the maximum tension of the film, so as its plastic deformation. The addition of clay has the film more durable and less brittle, one can see the drop in the maximum stress and plastic deformation.

Casariego, et al. (2009) observed that the values of the maximum tensile strength of films and chitosan clay increased significantly with increasing chitosan concentration, while the strain values decreased to values higher concentration of chitosan. The presence of clay in the results of Casariego et al (2009) did not appear to influence the properties of these two values.

Azeredo (2008) obtained similar results for the maximum tensile stress and plastic deformation to the results of Q2, and their chitosan films were microcrystalline cellulose as an additive. To solve this problem of low breakdown voltages, Azeredo (2008) used glycerol as plasticizer which improved the mechanical properties, but reduction in relation other key properties of the biofilm as the permeability to water vapor.

### Table 2 - Experimental results of maximum rupture stress and plastic strain for the films.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$\delta_{\text{max}}$ (MPa)</th>
<th>$\xi$ (%)</th>
</tr>
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<tbody>
<tr>
<td>Q1</td>
<td>24.1</td>
<td>3.6</td>
</tr>
<tr>
<td>Q2</td>
<td>50.2</td>
<td>4.4</td>
</tr>
<tr>
<td>Q1A</td>
<td>7.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Q2A</td>
<td>18.8</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Costa Jr. (2008) studied films of chitosan, poly (vinyl alcohol) as an additive and observed that the higher the concentration of chitosan in the mixture implies increasing the maximum tensile strength, a fact also noted by other authors studying the same mixtures.

Arvanitoyannis et. al. (1998) found similar results for biofilm chitosan / gelatin / sorbitol / water.

Lavorgna et al. (2010) found values of breakdown voltage for movies sobente chitosan 1% of 26.0 MPa and maximum deformation of 6.82%, values very close to those found in this experiment.

### Conclusion

In this work it was possible to evaluate the mechanical properties of films composed of chitosan and clay synthesized in different concentrations. It was possible to reach some conclusions: increasing the concentration of chitosan makes the film more resistant, the film consists of 2% chitosan showed better results for maximum rupture stress and plastic deformation, 50.2 MPa and 4.4%, respectively; the addition of clay disadvantage mechanical properties.

### Acknowledgements

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