BFE 2009

Proceedings of the
International Conference on
Bio and Food Electrotechnologies

22-23 October 2009
Compiègne, France

Edited by Eugène Vorobiev, Nikolaï Lebovka & Jean-Louis Lanoisellé
EFFECT OF MODERATE ELECTRIC FIELD IN THE PHYSICAL AND TRANSPORT PROPERTIES OF CHITOSAN COATINGS

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Abstract:

Edible films and coatings can provide additional protection for food, while being a fully biodegradable, environmentally friendly packaging system. Preliminary works have shown that the presence of a moderate electric field during the preparation of chitosan coating solutions may influence e.g. their transport properties. The aim of this work was to determine the effect of field strength on functional properties of chitosan coatings (obtained from lobster of the Cuban coasts). Four different field strengths (50, 100, 150, 200 V cm$^{-1}$) were applied during the preparation of the film forming solution, films were cast and, for each electric treatment, the water vapor, O$_2$ and CO$_2$ permeabilities of the films were determined, together with their solubility in water. The films were also analysed using scanning electron microscopy (SEM) and X-ray diffractometry (XRD). The results showed that the electric field has statistically significant effects on films’ transport properties (which e.g. for water vapour permeability, varied from 0.3228 to 0.2667 (g (m.day.atm)$^{-1}$)) and structure, a positive correlation having been found between the water vapor, O$_2$ and CO$_2$ permeability coefficients and the applied field strength. XRD indicated that when electrically treated, chitosan films exhibited a more ordered structure and a clearly higher crystallinity when compared with non-treated films. SEM micrographs evidenced that the surface morphologies of chitosan films were influenced by the electric field. In fact, the electric field treatment led to a structure with more regular layers as can be seen in the cross-sections of the films. These results clearly indicate that, when applied to the film-forming solution, the electrical field treatment may be a good tool to finely adjust the transport properties e.g. in taylor-made film formulations.

Key words: edible coatings, electric fields, transport properties.

1 Introduction

Edible coatings can provide an alternative to extend the post-harvest life of fresh fruits and other vegetables and can also result in a similar effect as modified atmosphere storage in modifying the internal gas composition (1). Indeed, this protective barrier can be formulated to prevent the transfer of moisture, gases, flavor or lipids, and thus to maintain or improve food quality and to increase food product shelf life (2). Chitosan has been widely used for the production of edible coatings and edible films (3,4,5). Chitosan films are excellent oxygen and
carbon dioxide barriers and have interesting antimicrobial properties (3,6). Ohmic heating is based on the passage of electrical current through a sample that has electrical resistance. The electrical energy is directly converted to heat and instant heating occurs, at a rate which depends on the intensity of the current passing through the material.

García et al, (2009) analyzed the effect of applying an electrical field during drying on the microstructure of films formulated with different concentrations of chitosan and methyl-cellulose; those authors have shown that the electrical field treatment could be a good alternative to improve film flexibility and to increase water vapor barrier properties.

In this context, the objectives of the present work were to analyze the effect of applying a moderate electric field to film-forming solutions of chitosan, to evaluate the films’ microstructure by SEM and X-ray diffraction and determine the effect of field strength on transport properties of chitosan coatings.

2 Materials and Methods

2.1 Coating Materials
The materials used to prepare the edible coating solutions were: chitosan (obtained in the Pharmaceutical Laboratories Mario Muñoz, Cuba) with a degree of deacetylation of 90% approximately, Tween 80 (Acros Organics, Belgium) as surfactant and lactic acid (90%, Merck, Germany).

2.2 Film Formation
The coating solutions were prepared dissolving the chitosan (1.5% w/v) in a 1% (v/v) lactic acid solution with agitation using a magnetic stirrer during 2 hours at room temperature (20 °C); subsequently, Tween 80 was added as a surfactant at a concentration of 0.1% (w/w) (4).

2.3 Device description
A set of experiments was conducted to determine the effect of the application of a moderate electric field to chitosan solutions. The chitosan solution samples were treated in an ohmic heater using four different field strengths (from 50 to 200 Vem⁻¹) (8).

2.4 Characterization of chitosan films
2.4.1 Conditioning and Thickness
All chitosan films used for permeability tests were conditioned in desiccators, at 20 °C and 25 % RH. Film thickness was measured with a hand-held digital micrometer (Mitutoyo, Japan) having a sensitivity of 0.001 mm. Ten thickness measurements were taken on each testing sample in different randomly chosen points and the mean values were used in permeability calculations.

2.4.2 Gases Permeability
Oxygen permeability (O₂P) and carbon dioxide permeability (CO₂P) were determined based on the ASTM (2002) method.

2.4.3 Water vapor permeability measurement and Film Solubility
The water vapor permeability (WVP) of the films was determined gravimetrically based on the ASTM E96-92 method (9, 10). The film solubility in water was determined according to the method reported by Gontard et al. 1994 (11).
2.4.4 Scanning electron microscopy (SEM)
Scanning electron microscopy (SEM) analyses were performed with a scanning electron microscope (Nova NanoSEM 200, The Netherlands) with an accelerating voltage varying from 10 to 15 kV.

2.4.5 X-ray diffraction and Crystallinity
X-ray diffraction patterns of the films were analyzed between 2θ = 4° and 2θ = 60° with a step size 2θ = 0.02° in an X-ray diffraction instrument (Bruker D8 Discover, USA). The crystallinity index (CI) was defined using the equation CI = (I_{110} – I_{am})/I_{110} (12), where I_{110} is the maximum intensity (2θ, 20°) of the (110) lattice diffraction and I_{am} is the intensity of the amorphous diffraction (2θ, 16°).

3 Results and Discussion

3.1 Oxygen permeability (O2P); Carbon dioxide permeability (CO2P); Solubility in water and Water Vapor Permeability
Table 1 shows O2P and CO2P as measured for chitosan films formed from solutions subjected to electric fields of different intensities. The samples with treatments made at 1014 V·cm−1 or higher have lower values (p < 0.05) of O2P and CO2P.

<table>
<thead>
<tr>
<th>Electric field strength</th>
<th>Solubility (%)</th>
<th>WVP (g·(m·day·atm)−1)</th>
<th>CO2 Permeability 10^14 (g·m·(Pa·s·m²)−1)</th>
<th>O2 Permeability 10^16 (g·m·(Pa·s·m²)−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 V·cm⁻¹</td>
<td>39.48±0.01a</td>
<td>0.3228±0.027a</td>
<td>6.98±0.030a</td>
<td>10.60±0.420a</td>
</tr>
<tr>
<td>50 V·cm⁻¹</td>
<td>39.42 0.03a</td>
<td>0.3219±0.022a</td>
<td>6.97±0.029a</td>
<td>10.60±0.450a</td>
</tr>
<tr>
<td>100 V·cm⁻¹</td>
<td>39.30±0.01a</td>
<td>0.2740±0.027b</td>
<td>6.74±0.037b</td>
<td>9.54±0.400b</td>
</tr>
<tr>
<td>150 V·cm⁻¹</td>
<td>39.28±0.01a</td>
<td>0.2728±0.030b</td>
<td>6.72±0.041b</td>
<td>9.42±0.540b</td>
</tr>
<tr>
<td>200 V·cm⁻¹</td>
<td>39.27±0.02a</td>
<td>0.2667±0.025b</td>
<td>6.72±0.040b</td>
<td>9.62±0.600b</td>
</tr>
</tbody>
</table>

*Different letters in the same column correspond to statistically different samples (p < 0.05).

Tab 1: Values obtained from water vapor permeability (WVP), CO2 permeability and O2 permeability for the films obtained with film-forming solutions subjected to different field strengths.

Wan, et al 2003 (13) observed that the crystallinity of the chitosan membranes increased gradually with increasing degree of deacetylation ranging from 70 to 90 %. This can be attributed to the fact that chains of chitosan with higher degree of deacetylation are more compact thus facilitating hydrogen-bonding formation and consequently favoring crystallinity formation in the film. Furthermore, chitosan with a higher degree of deacetylation contains more glucosamine groups, which also facilitate the hydrogen-bonding formation; on the contrary, chitosan with a lower degree of deacetylation has more acetyl groups, which hinder the chitosan chain packing due to their rigidity and steric effect (14).

The results obtained in this work show that WVP of chitosan films decrease with the increase of the field strengths for values of 100 V·cm⁻¹ or higher (Table 1).

Anker, et al 2000 (15) concluded that the reason for the increased WVP is probably the larger pores formed at high polymer concentration, compared to the smaller pores formed at low polymer concentration. The work of Miller and Krochta 1997 (16) also points at the fact that the permeability is highly affected by how closely packed the polymer chains are, thus establishing a direct relationship between the crystallinity of the structure and permeability. In the present work the solubility of the chitosan films was evaluated, and it is shown that the
solubility of chitosan films decrease with the increase of the field strengths for values of 100 V·cm⁻¹ or higher (Table 1). Balau et al. (2004) showed that the electric field plays an important role in the crystallization process, which may also interfere in the water solubility of the films.

3.2 X-ray diffraction

Figure 2 shows that the crystallinity of the chitosan films increases gradually with the increase of the electric field strength. This indicates that, during the moderate electric field treatment, a structure with a different X-ray diffraction pattern was developed. This may be attributed to the fact that the chitosan chains with higher degree of deacetylation are more flexible. Flexible chains will facilitate the hydrogen bond formation and consequently crystallinity formation in the film. In addition, there was one other diffraction peak at around 8°-10° (2θ).

Fig. 1: X-ray diffraction patterns of chitosan films to (-) Control (-) Conventional heating (-), Electric fields 100 V cm⁻¹ and (-) Electric fields 200 V cm⁻¹

Results indicated that the application of a moderate electric field to the film-forming solutions had significant effects on the crystallinity index (CI), which was higher for films treated with electrical fields.

3.3 Scanning electron microscopy (SEM)

When their film-forming solutions were submitted to an electric field, chitosan films have shown crystals in their structure, evidencing that there must have been morphological influences from that treatment. In fact, the electric field treatment lead to a structure with more regular layers as can be observed in the cross-section images of Figure 2.

The development of films with a uniform and compact layer can be an important achievement towards the improvement of various film properties, such as their permeability to gases.
The search for homogeneous structures thus becomes a target of the research involving edible films. In this perspective, the application of electric fields may provide an interesting solution for that problem and has gained importance in this area of research. Garcia et al. (2009) showed that the surface morphologies of films were influenced by the preparation method, indicating that the application of an electric field during drying was an influencing factor. SEM analyses indicated that this treatment led to a more regular structure.

Fig 2: SEM micrographs of chitosan films and cross-section to (a) control, (b) conventional heating, (c) electric fields 100 V cm$^{-1}$, (d) electric fields 200 V cm$^{-1}$. 
References


