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Barrier, mechanical and morpho-structural properties of gelatin films with carbon nanotubes addition

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ABSTRACT

The effect of a small amount of carbon nanotubes (CNT) on the water content and physical properties of gelatin films with glycerol were evaluated. Control films and those with 0.001% (w/w) CNT addition were prepared. Water isotherms adsorption and water vapor permeability, were undertaken on the gelatin films to asses barrier characteristics. Tensile strength and elongation at break were evaluated with a texture meter, while hardness and elastic modulus were measured with a nanoindentation tester, all these tests were measured at 22%, 40%, 58% and 75% RH. Atomic force, environmental and field emission scanning electron microscopy, were used to see the films morpho-structure. The data adsorption isotherms fitted well all models tried. An increase in RH decreased the tensile strength, and increased the elongation at break of all films. The CNT addition did not affect significantly the films barrier properties ($p > 0.05$), but it caused an increase of about 11.36% on the elongation at break of films, at any RH higher than 40%; with no effect on the tensile strength and hardness. Films image analysis, showed a morpho-structure with high ordering, which might well correlate with CNT addition to the protein matrix. CNT were found embedded in the polymeric matrix.

1. Introduction

Different raw materials have been used to prepare biodegradable films, being common the biopolymers from renewable sources such as gelatin, one of the first materials used to obtain films, which is still being employed because of its abundance, low production cost, world-wide accessibility and easy handling during films production (Vanin et al., 2005).

The gelatin is a water soluble protein, obtained from collagen by acid or basic hydrolysis, depending on the hydrolysis degree, it has a molecular weight from 65 to 300 kDa; being composed mainly of glycine, proline and 4-hydroxyproline. This macromolecule is used in a lot of applications; e.g., as gelling agent, dispersant, medicine encapsulator and potentially, in new biodegradable package formulations (Peña et al., 2010). In this last case, the addition of plasticizers is needed to decrease the brittleness of gelatin films, which act by reducing intermolecular forces, promoting an increase in the mobility of the constitutive polymeric chains and improving the flexibility. Polyols (e.g. sorbitol, xylitol, and glycerol) are often used as protein plasticizers, been glycerol perhaps the most widely used.

Usually, protein films are excellent aroma and oxygen barriers. However, due to its hygroscopic nature, they tend to absorb high water fractions at high relative humidity (HR), as a consequence, an over-plasticized film matrix with weak mechanical and barrier properties may be obtained (Lim et al., 1999).

It has been found that multiwall carbon nanotubes (CNT), show mechanical properties of their own, e.g., an elastic modulus of about 0.91 TPa, and a tensile strength of 0.15 TPa, have been previously reported, making them suitable to reinforcing materials in ceramics, metals and polymers (Demczyk et al., 2002). Thus, the addition of nanoparticles as nanominerals, cellulose nanocrystals or carbon nanotubes to biopolymer films, has a great potential to improving its mechanical and thermodynamic properties, for instance, it has been reported an increase of hardness and Young modulus in the manufacture of polyhydroxyalkanoate films when using CNT (Yun et al., 2008). Also, on the one hand, it has been found an increase in the tensile strength by addition of montmorillonite to gelatin films (Bae et al., 2009; Martucci and Ruseckaite, 2010; Rao, 2007). On the other hand, the addition of cellulose nanocrystals decreases the hydrophilic character of gelatin films, and improve its mechanical properties (George and Siddaramaiah, 2012).

Since water is the most ubiquitous plasticizer of hydrophilic polymers, which are commonly used to prepare films, it is important to analyze its aggregation state and the quantity present in the

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mentioned materials, in order to evaluate its effects on the film properties (Rivero et al., 2010). So, it is essential to know the effect of the water content to predict the film behavior on its final application, to achieve this, it is important to obtain the isotherms of water adsorption or desorption, which indicate the amount of water retained by a material as a function of the surrounding RH, measured as the water activity (a_w); which is a dimensionless parameter that relates the water vapor partial pressure of the material tested, over the pure water vapor partial pressure at equilibrium (Rahman, 2006). In consequence, film barrier characteristics, in combination with especially film mechanical properties, should be measured to understand some of its functional behavior and possible applications.

In addition, microscopy plus digital treatment of images, may provide various parameters related with the morpho-structure of the matrix components (e.g. protein and polysaccharides) in films. In this sense, atomic force, field emission and environmental scanning electron microscopy, might prove useful tools to characterizing films morphology.

With the development of nanotechnology, nanomaterials have wide application in various areas (e.g. medicine, chemical industry, materials design, and electronics). Carbon nanotubes (CNT) are an example of a carbon-based nanomaterial, whose unique properties have sparked great popularity in nanotechnology. However, precise information about the toxicity of CNT in vivo is still poor or contradictory, being still recommended the use of low concentrations in bio-experiments (Liu et al., 2008).

As is known, gelatin in solution has a "random coil" type structure, which may allow its interaction with nanoparticles, modifying its physical properties. However, no reports have been found on the use of CNT as nanostructural materials to reinforce gelatin films.

Thus, the objective of this work was to evaluate the effect of CNT addition in gelatin films on its water content, barrier and morpho-structural properties, as well as its mechanical properties at various relative humidities.

2. Material and methods

2.1. Material

Various materials were used in this work: commercial type "B" bovine gelatin with 290° Bloom (Duche, México); analytical grade glycerol (Fermont, México); multiwall CNT (made in China) and analytical grade sodium dodecyl sulphate (SDS) (Reasol, México). The following analytical grade salts (Fermont, México) were used to prepare saturated solutions: lithium chloride (LiCl), potassium acetate (CH_3 COOK), magnesium chloride ($MgCl_2$), potassium carbonate (K_2CO_3), magnesium nitrate ($Mg(NO_3)_2$), sodium bromide (NaBr), potassium Iodine (KI), sodium chloride (NaCl), potassium chloride (KCl), potassium nitrate (KNO_3). Analytical grade phosphorus pentoxide (P_2O_5) was purchased from Sigma Aldrich.

2.2. Gelatin films manufacture

Considering the probable CNT toxicity in materials for food applications, with reports meaning that even small quantities of CNT (weigh/area rates as low as 22.6 μg/cm^2), might already have potential toxic effects (Liu et al., 2008) and also, previous works undertaken at the same institution (Sifuentes, 2011), where the same three different low concentrations of both CNT and SDS (0.001%, 0.002% and 0.004% w/w) were used, with no optimum combination CNT–SDS for an adequate CNT dispersion found within the above concentration range; it was decided for this work, to use the lowest CNT concentration, but increasing the amount of SDS, seeking for the effect on its film properties. Thus, a solution containing 0.001% (w/w) CNT (equivalent to 0.1 g CNT/100 g gelatin) and 0.1% (w/w) SDS was prepared using distilled water, this was put at once into an ultrasonic water bath at 60 °C for 4 h. A filmogenic solution with 9% (w/w) gelatin and 3% (w/w) glycerol was prepared with distilled water, at 60 °C with continuous agitation using a magnetic stirrer. The two above mentioned solutions were mixed and put into the ultrasonic water bath at 60 °C for 1 h. Then, the resulting filmogenic solution was poured on squared Petri dishes with 529 cm^2 of surface (23 × 23 cm), and dried in an oven at about 45 °C during 24 h. Afterwards, the films were detached from the plates, and stored in a desiccator for 7 days at room temperature and a RH of 57%, provided by a saturated solution of NaBr (Mali and Grossmann, 2003). The control film was obtained following the same procedure as the one mentioned above, except that neither CNT solution nor SDS were added to the filmogenic solution.

2.3. Film thickness

Film thickness measurements were undertaken 10 times along the samples, with a micrometer (Mitutoyo Corp., Tokyo, Japan). The thickness mean values were used in the determinations of the films barrier and mechanical properties.

2.4. Water vapor adsorption isotherms

The method proposed by Spiess and Wolf (1987) was followed. Round pieces of films were cut with the same size as the container (radio of 2.5 cm) and taken to a minimum moisture, by putting them into a desiccator with phosphorous pentoxide (P_2O_5) during 90 days. The samples were placed at 25 ± 0.5 °C employing a series of individual sealed containers, which had a known RH provided by saturated salt solutions. The sealed containers equilibrium was measured using an apparatus that measures water activity (Aqualab model 4TE, Pullman, Washington, USA). Tymol was added to equilibrium cells with RH higher than 70%, to prevent fungi growth during storage. Every 7 days, the samples were weighed till the mass loss or mass gain was about 0.001 g in two consecutive weighs. Once the equilibrium had been reached, the moisture content was measured using gravimetric analysis, by drying the sample in an oven at 70 ± 1.0 °C during 24 h, to determine the solid mass content. For every RH, each test was done three times with two replicates per test (n = 6).

2.5. Modeling of the water adsorption isotherms

To carry out the adsorption isotherms of the nanostructured gelatin films, the following models were used (Sablani et al., 2002):

The Lagmuir model:

$$M = \frac{M_{0L} C_L a_w}{(1 - C_L a_w)} \tag{1}$$

where M is the water content, a_w is the water activity, M_{0L} is the theoretical monolayer moisture content and C_L is an energy related constant.

The Brunauer, Emmett and Teller (BET), model:

$$M = \frac{M_{0B} C_B a_w}{(1 - C_B a_w)} \left[\frac{1 - (j+1) a_w^j + j a_w^{j+1}}{1 + (C_B - 1) a_w - C_B a_w^{j+1}} \right] \tag{2}$$

where M_{0B} is the theoretical monolayer moisture content, j is the number of water layers adsorbed on the material surface, C_B is a dimensionless parameter related with the adsorption heat of the monolayer.

The Guggenheim, Anderson and De Boër (GAB), model: