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ACTIVE PACKAGING TO PROLONG THE SHELF LIFE OF MOZZARELLA CHEESE

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ABSTRACT

The main targets of our work were (1) to test an active packaging of poly vinyl alcohol (PVA- degree of hydrolysis (DH) = 98,0-98,8%) for mozzarella cheese; (2) tested the effect of silver nanoparticles (NP) as a bactericidal agent in order to reduce decay of fresh cheese and; (3) to study the solubility and mechanical properties (puncture force) of PVA films. This study evaluated the effect of coating produced from PVA and glycerol as plasticizer on cheese conservation (41°F (5 ±2°C)). Silver nanoparticles (NP) were obtained by the reduction of the silver ion (Ag+). The size control and the stabilization of the NP can be obtained using determined stabilizers which prevent nanoparticles aglomeration and consequent precipitation. In this work, silver nanoparticles were obtained by reducing silver ions with $NaBH_4$; then, they were stabilized in the presence of poly(vinyl alcohol) (PVA- degree of hydrolysis (DH) = 86,7 - 88,7) and gamma radiation, for cobalt-60 (^{60}C0), when subjected to dose of 5 kGy. PVA films produced have good mechanical properties and potential application for food packaging. The active packaged presented higher acceptance, lower weight loss rate during storage time and an extended the usable life of cheese, when compared to the control (without PVA films) without affecting the functional microbiota of the product. Puncture force (PF) of films increased with increasing glycerol concentration (P0.05). Nanoparticles with diameters smaller than 5 nm were formed when silver ions were reduced with $NaBH_4$ (and stabilized with gamma radiation – 5kGy).

1. INTRODUCTION

Recently, new food-packaging systems have been developed as an answer to trends in consumer preferences towards mildly preserved, fresh, tasty and convenient food products with a prolonged shelf-life. Active packaging changes the condition of the packaged food in order to extend shelf-life or improve food safety or sensory properties, while maintaining the quality of the packaged food [1]. Nowadays, a lot of attention has been given to biodegradable polymers, such as poly vinyl alcohol (PVA), which is biodegradable, non-toxic synthetic and presents high tensile strength and flexibility, as well as high oxygen and aroma barrier properties [2,3]. The addition of a plasticizer agent to films is required to overcome film brittleness, caused by high intermolecular forces. Plasticizers reduce these forces and increase the mobility of polymer chains, thereby improving flexibility and extensibility of the film. On the other hand, plasticizers generally decrease gas, water vapor and solute permeability of the film and can decrease elasticity and cohesion [4,5]. Silver nanoparticles (NP) were obtained by the reduction of the silver ion (Ag+). The size control and the stabilization of the NP can be obtained using determined stabilizers which prevent nanoparticles aglomeration and consequent precipitation. In this work, silver nanoparticles were obtained by reducing silver ions with $NaBH_4$; then, they were stabilized in the presence of poly(vinyl alcohol) (PVA) and gamma irradiation. We have used X-ray diffraction (XRD) and UV–Vis spectroscopy to characterize the nanoparticles obtained.

2. EXPERIMENTAL

2.1. Materials. The following materials were used to prepare the film: poly vinyl alcohol (PVA) - Celvol® 350 (GH = 98.0-98.8%) - (synth), glycerol (synth), $AgNO_3$ (synth) and $NaBH_4$ (synth). Polyethylene film for domestic use (fischer S.A).

2.2. Methods

2.2.1. Sample Preparation. The PVA films were produced by casting process (dehydration of a filmogenic solution) from solutions of PVA (5.0g), glycerol (0.3g) in water (100mL). The solution was heated to 140ºF (60°C) to dry and then a transparent film was formed.

2.2.2. Gamma Irradiation. Samples were irradiated at room temperature in air, in Co-60 irradiator with 700.000 Ci activities, operating at 5.0kGy.h^{-1} (dose rate of 5kGy).

2.2.3. Mechanical Properties. The force of the film was determined in puncture tests [4]. The films were fixed in a 33 mm diameter cell and perforated by a 3 mm diameter probe, moving at 1 mm/s. These tests were accomplished with an instrument of physical measures TA.XT2i (SMS, Surrey, UK). The puncture force (F) was determined with the software Texture Expert V.1.15 (stable systems micron) directly from the force *versus* displacement curves. The films have been equilibrated at a 25ºC and 60% relative humidity (RH) for 2 days prior to measurement. A commercial polyethylene film was also measured to compare the mechanical properties to PVA films. The results are the average of four samples.

2.2.3. Water Vapor Transmission (WVT). The WVT was determined according to ASTM E96-80 [6] modified by Gontard et al. [4]. A container with silica gel was closed with a sample of film firmly fixed on top. Then the container was placed in a desiccator with distilled water at a temperature of 25.0^{o}C. The films were weighed daily on a Mettler analytical balance during 10 days. Water vapor transmission (WVT) was calculated according to equation 1:

$$WVT = \frac{\bar{v}.x}{A} \qquad (1)$$

Where WVT is Water Vapor Transmission (g H_2O. mm.cm^{-2}), x is the average thickness of the film (0.055 ± 0.010 mm) and A is the permeation area (23,76 cm^{2}).

2.2.4. Solubility in water. Solubility was measured by submerging two pre-weighed film samples for 15 minutes at room temperature. Afterwards, the films were dried to constant weight at 131ºF (55°C). The solubility of each film was determined according to the expression (2):

$$\% MS = 100 \times (M_i - M_f) / M_i \qquad (2)$$

Where %MS is percentage of soluble mass, M_i is initial mass of the film and M_f is final mass of the film.

2.2.4. UV-Vis Spectroscopy. UV-Vis spectra were obtained on a UV-Vis spectrometer Shimadzu UV-2401 model at a range 200-800nm.

2.2.5. Film thickness. Film thickness was measured with a micrometer with a sensitivity of 0.001 mm. Five to ten thickness measurements were taken for each film, and the averages were taken as the results.

3. RESULTS

The PVA and PVA/glycerol films are transparent enough, with good mechanical properties and potential application for food packaging. PVA films with NP showed more yellowing (see figure 1). Solubility and puncture force of PVA films with NP are shown in table 1. A commercial polyethylene film was also measured to compare the mechanical and barrier properties to PVA films.

(a) **(b)**

Figure.1. Illustrative picture of (a) PVA / glycerol / NP film and (b) polyethylene film after six days.

As it can be seen in table 1, the mechanical characteristics (puncture force) are influenced by NP concentration: an increase in NP concentration resulted in a considerable increase of the puncture force and of the films, whereas WVT can be significantly reduced applying low NP concentrations (Fig. 2).

Table 1. Mechanical properties and solubility of the PVA films.

Film	Solubility	Puncture Force (N)
PVA	20.69±1.44	43.18
PVA/NP 0.5 mM	20.37±1.35	51.35

PVA/NP 1.0mM		65.38
PE	insoluble	4.85

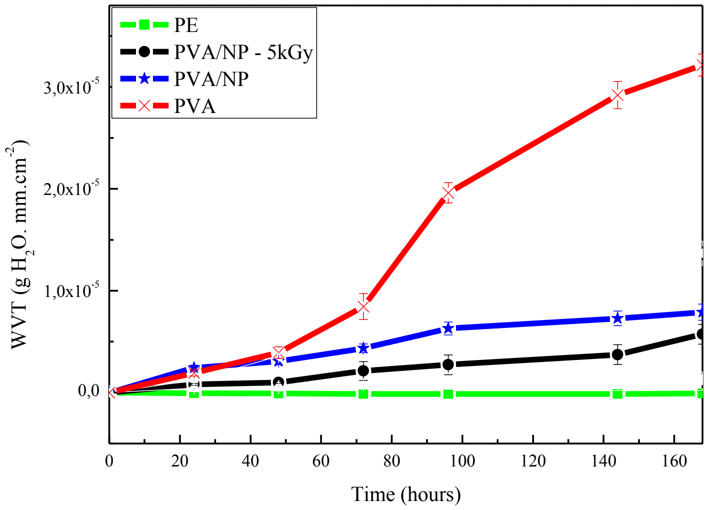

Figure.2. Barrier properties of PVA films, PVA-NP (PVA with silver nanoparticles (NP)) and PE (commercial polyethylene film). WVP = water vapor permeability.

The structure of prepared silver nanoparticles has been investigated by X-ray diffraction (XRD) analysis. The XRD study indicates the formation of silver (Ag) nano particles. The peaks around 3.40 keV, 22 keV and 25 keV are correspond to the binding energies of AgL, Ag Ka1 and Ag Ka2, respectively. The UV/Vis absorption spectra of the silver nano particles dispersed in water is shown in the fig. 3. The formation of the silver nanoparticles was monitored using UV-Vis absorption spectroscopy. The UV-Vis spectroscopy revealed the formation of silver nanopartícles by exhibing the typical surface plasmon absorption maxima at 410 nm from the UV–Vis spectrum. The stability of silver nanoparticles was observed for 1 year and it shows a peak at the same wavelength.

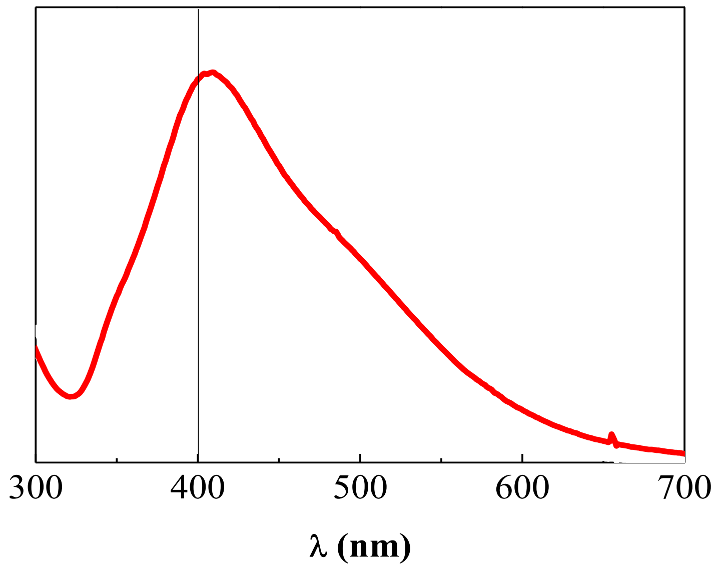

Figure.3. (a) UV/Vis absorption spectra of Ag nano particles.

The presence of plasticizer causes a reduction of intermolecular interaction and also increases the mobility of macromolecules [4], leading to the increase in puncture force (PF) of films. The result was in accordance with Gontard et al. [4] who observed that PF of gluten films increased from 6 to 20% with increasing glycerol concentration from 16 to 33g glycerol/100g dry matter. There was no significant difference for the solubility values when compared to the PVA/glycerol and PVA/glycerol/NP films (P>0.05). PVA films had been reported to be ineffective moisture barriers due to their hydrophilic nature [7], [8]. PVA and PVA/NP films, prepared by casting process, were examined for biodegradation by composting over 60 days (Fig. 4).

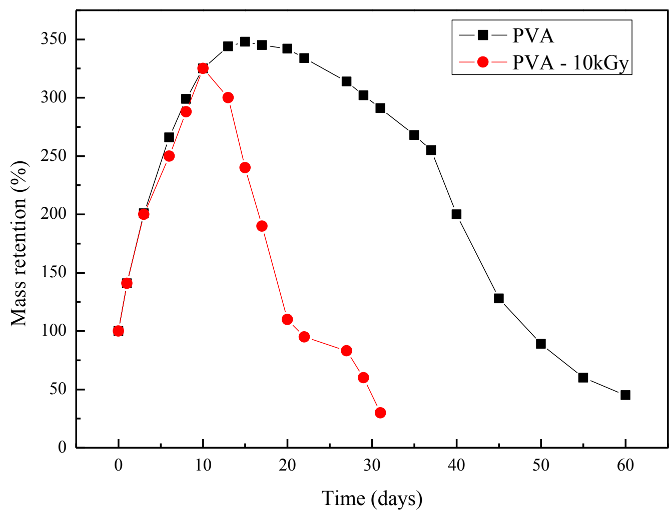

Figure 4. - Biodegradation curves of PVA films (0 and 10kGy) in simulated soil.

Biodegradation of non-irradiated PVA was relatively slower, with losses of 45% after 60 days compared to the PVA irradiated with 10kGy (30% after 30 days). This is probably due to the film degradation at this level dose. Puncture force of PVA films irradiated with 10kGy (38.5N) were significantly lower when compared to the PVA non-irradiated film (43.18N). The UV-Vis spectrum of PVA films (10kGy) showed an increase of the absorption intensity in the range of 260-340 nm, related to carbonyl groups. Campos and Franchetti [9] also observed a significant increasing of the absorbance intensity of carbonyl groups (260-340nm) and the presence of three sharp bands related to the absorption of different types of carbonyl groups of biotreated poly(ε-caprolactone) – PCL films, suggesting the degradation at this level dose.

Cheese mozzarella stored under atmospheric conditions had a shelf life of only 30 days (in PE packaging) which was mainly limited by its sensory acceptance and microbial spoilage. In the present work, we tested the effect of silver nanoparticles (NP) impregnated in plastic film of PVA and PVA/NP (PVA film with silver nanoparticules) to reduce decay of cheese mozzarella which were stored without plastic films (control fruits) and in PVA, PVA/NP and PE packaging at 41°F (5±2°C) during 90 days. The thickness of PE, PVA/NP and PVA packaging were 0.40 ± 0.010 mm.

The active packaged (with NP) cheese presented higher acceptance, lower microbiological growth, lower weight loss rate during the storage time and an extended shelf-life, as compared to the control cheese (without plastic films). The cheese under PVA films with NP presented shelf life of 90 days showing good sensory acceptance throughout the storage period. The cheese stored in PE had less mass loss than the ones wrapped in PVA films and also when compared to the ones with no packaging at all. The PVA/NP films are the most effective in cheese storing because they are less permeable to the water vapor when compared to the PVA films (Fig. 2). It explains why the cheese wrapped with PVA/NP had less mass loss and still presented the active ingredient that extends the cheese shelf-life. In 90 days, in 41°F, a significant increase in the humidity of cheese in polyethylene was observed while no significant differences were noted with PVA/NP packaging.

3. CONCLUSIONS

-Addition of polyol (glycerol) to the PVA films resulted in plasticization of the polymer matrix.
-PVA film with silver nanoparticles was able to extend the usable life of cheese in 90 days.
-Films from PVA formulated with NP had good performance of flexibility and low solubility, indicating potential application as active packaging.

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