Bionanocomposites: a novel alternative preservation

Bionanocompuestos de quitosano-óxido de grafeno: una alternativa novedosa para la conservación de alimentos

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Abstract

The bionanocomposites are an emerging alternative to a new era of materials with excellent mechanical properties, thermal, gas permeability and moisture, but above all, biodegradable and bio compatible. In this research, pack- aging synthesis was studied from graphene oxide -chitosan nanocomposites and its potential application in the food packaging industry. Nanocomposites were pre- pared by a thermal cross linking reaction between chitosan and graphene oxide at 120 °C. The mechanical properties of the films obtained were studied, where it was observed that the mechanical strength increased from 1.2 to 22.7 ± 6471.6 ± 1775.5 MPa when 0.1 % of GO was added to the films. Similarly, the increased stability of the packaging was evidenced by the increase in thermal stability, as evidenced in the gradual increase in glass transition temperature (Tg) with increasing the GO. Finally, the antimicrobial properties of the films were evaluated against E. coli K-12 MG 1655 (Gram-negative) and B. subtilis 102 (Gram-positive). The CF-GO sheet with 0.6 % had the highest inhibition against *E. coli* and *B. subtilis*, with 22.86 % and 54.93 % inhibition, respectively. Thus, the addition of GO within the films significantly increased the thermal and mechanical stability and added antimicrobial properties, which makes the use of these films in food preservation industry have a great prospect.

Keywords: nanocomposites; gas permeability; antimicrobial properties.

Introduction

Currently, a lot of materials used in the packaging industry are not biodegradable, which generates a high quantity of contamination due to its accumulation in the planet, this, affecting the life of many organisms. For this reason, biopolymers have been used, looking to mitigate the environmental contamination problem and the preservation of food at the same time. However, the biopolymers are well known in for its poor mechanical barrier properties against humidity and thermal stability, raising the costs to the production and processing (Bharadwaj, 2001; Koh et al., 2008; Pandey et al., 2005; Scott, 2000; Sorrentino, Tortora, & Vittoria, 2006), which has been tried to solve using fillings to generate composite materials. Currently, the use of nanofillings is a topic of great interest, since when the dimensions of the filling is reduced, the possibility of interaction with the polymeric matrix is maximized notably improving the properties. Of the material in a higher interaction between the two phases (Weiss, Takhistov, & McClements, 2006). Additionally, the nanofillings can provide additional properties, such as antioxidant properties, antimicrobial properties, protection to ultraviolet light degradation, immobilizing enzymes, degradation sensors, etc., making them very attractive to the food industry (Azeredo, 2009; Rhim, Park, & Ha, 2013; Sorrentino et al., 2006; Sorrentino, Gorrasi, & Vittoria, 2007). Inside of the most studied bionanocomposites for food packaging, we find starch and cellulose derivatives, polilactic acid, butylene polisuccinate and polyhydroxybutyrate. On other hand, the most used nanofillings have been the silica nanoclays, such as montmorillonite and the kaolinite (Suprakas Sinha Ray & Bousmina, 2005). A great challenge that still is present, is to achieve an excellent dispersion and compatibility with the nanofillings inside a continuous polymeric phase (Rhim et al., 2013). The nanocomposites are mixtures with the organic and inorganic additives that have at least one nanometric scale dimension, with different geometries (Spheres, fibers, particles) that generate a performance improvement of the mechanical properties, against different gases and solvents, apart from decreasing density, improving transparency, flux and the possibility to be reused, giving great advantages in front of composite material or pure polymers (Alexandre & Dubois, 2000; Santos et al., 2012; Giannelis, 1996; S. Sinha Ray & Okamoto, 2003). On other hand, the excellent physical, mechanical and optical properties of the nanomaterials deriving from the graphene, such as the graphene oxide make them very attractive to be used as nanofillings in nanocomposites with biopolymers such as chitosan, to increase the mechanical, thermal and barrier properties. Additionally, the nanomaterials deriving from graphene, have demonstrated that they have excellent antimicrobial properties that will be added in the nanocomposite in which it will be introduced, Table 1 (Stankovich et al., 2006).

Table 1. Surface and mechanical properties of the nanocomposites films

Sample (% OG)	Contact angle (°)	Thickness (μm)	Breaking resistance (Mpa)	Stretching (%)	Young's Modulus (Mpa)
0	88.53 ± 2.38 a	48 ± 4.2 b	32.4 ± 6.2 c	8.4 ± 1.2 a	22.7 ± 1.2 b
0.1	91.28 ± 3.39 a	52 ± 6.9 b	52.0 ± 22.4 b	0.9 ± 0.8 b	6471.6 ± 1775.5 a
0.25	89.58 ± 2.24 a	54 ± 4.8 a.b	69.6 ± 15.9 a	1.5 ± 1.9 b	6879.0 ± 2011.7 a
0.4	91.84 ± 3.97 a	59 ± 4.9 a	62.7 ± 21.2 a	3.0 ± 2.2 b	5936.3 ± 1112.8 a
0.6	93.43 ± 1.94 a	65 ± 9.4 a	43.2 ± 14.8 a	0.9 ± 0.3 b	5843.7 ± 1485.0 a

Source: The authors.

Methodology

All the reactives were acquired from Aldrich, unless otherwise stated. The graphene oxide was prepared by a modified method of Hummers as it was previously reported (Santos et al., 2012). The chitosan films were prepared according with the method reported by Shao et al. (2013), modifying the cross-linking temperature from 100 to 120 °C. only, and adding the necessary quantity of graphene oxide to complete the 0.1, 0.25, 0.4 y 0.6 % (p/p) concentrations in relation to the chitosan. The characterization was held through infrared spectroscopy (data not yet published) (spectrometer Agilent Cary 680 FTIR) and the mechanical properties were determined with a mechanical analyzer (Shimadzu EZ-LX, Japan), under the ASTM D882-12 parameter. Finally, the antimicrobial properties were determined with the help of a fluorescence microscope, through the method of dead and alive cells counting (Santos et al., 2012). The film's thickness was determined using a digital Mitutoyo Digimatic micrometer. The superficial properties were determined through the static aqueous contact angle technique (KSV CAM 200 instrument, KSV Ltd.).

Results

The effective dispersion of the nanofillings in the polymeric matrix and the material homogeneity can be seen in the results done by the mechanical tests, the thickness and contact angle, since it is observed that the matrix keeps its hydrophobic nature despite the presence of the GO, which explains why the hydrophobic covalent bonds that are formed between the epoxide groups of the GO and the amino free of chitosan, besides, reinforce the material as it is seen in the rise of the breaking resistance of 32.4 ± 6.2 to 52.0± 22.4 MPa between the chitosan without GO and the chitosan with 0.1 % of GO, although a noticeable decrease of the material stretching is also observed.

The shown data are the mean of six analyses with its respective standard deviation. The means of the analyses were compared through a Duncan Multiple Range Test. The values with different letters in a same column are meaningfully different (α: 0,05).

The antimicrobial activity of the chitosan/graphene oxide films is determined with the analysis of alive and dead cells with a fluorescent microscope regarding *E. coli* and *B. subtilis* bacterial strains. As observed in Table 2, the highest inactivation percentages were obtained as the graphene oxide quantities were raised in the CF-GO nanocomposite films (0.4 and 0.6 %). The highest inactivation was obtained with the CF-GO (0.6 %) *E. coli* (22.83 %) and *B. subtilis* (54.93 %).

Table 2. E.coli and B. subtilis inactivation percentage with CF-GO nanocomposite films

	Inactivation percentage (%)	
Sample(% GO)	*Escherichia coli*	*Bacillus subtillis*
0	1.04 ± 1.61 d	1.25 ± 1.42 d
0.1	3.09 ± 2.98 d	N.D.
0.25	7.09 ± 2.73 c	7.51 ± 2.54 c
0.4	12.21 ± 4.6 b	22.69 ± 7.93 b
0.6	22.83 ± 4.48 a	54.93 ± 13.35 a

Source: The authors

The presented data are the average of 18 analyses of analysis with its respective standard deviation. The averages of the analysis were compared through the Duncan Multiple Range Test. The values with different letters in a same column are meaningfully different.

Conclusions

In this work, films of the chitosan/graphene oxide nanocomposite were prepared effectively, which mechanical properties and thermal stability were much higher than the chitosan without the nanofilling. The results of the analysis of the breaking resistance show us a high increase with the introduction of GO, although with a sacrifice of elasticity, which is a reflection of an excellent dispersion and interaction of the nanofilling with the polymeric matrix in the nanocomposite. On other side, the antimicrobial analyses show that it possesses a great inhibition capacity against *E. coli* and *B. subtilis* bacterial strains, being this inhibition dependent of the quantity of graphene oxide present in the film. In future works, the microbial inhibition mechanism of the material will be explored, with the goal of confirming its application in the industry of food packaging.

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