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Spectroscopic analyses of the influence of electron beam irradiation doses on mechanical, transport properties and microstructure of chitosan-fish gelatin blend films

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ABSTRACT

The objective of this work was to better display the effect of electron beam accelerator doses (0, 20, 40 and 60 kGy) on structural, mechanical and barrier properties of edible lightly plasticized chitosan-fish gelatin blend film. From Electron Spin Resonance (ESR), signal at 3500 G for blend film was identified as free radical formation during irradiation, which might introduce intermolecular cross-linking into the polymer matrix, thus affecting structural properties. Tensile Strength (TS) for gelatin film significantly increased with growing irradiation doses (improved by 30% for 60 kGy), but the TS of chitosan and blend films were not significantly affected. On the contrary, irradiation significantly reduced elongation at break (%E) for chitosan and blend film up to 50% whereas it twice increased the Young modulus. Moisture barrier efficiency (30–84% RH gradient) of blend films was slightly improved after irradiation. Oxygen permeability also decreased after 60 kGy irradiation treatment, for both chitosan and blend films. Surface hydrophobicity tended to decrease after irradiation. From Fourier Transform Infra-Red (FTIR) spectra, some noticeable differences were observed after irradiation, in the relative intensity and position of bands in the region between 3600 and 2800 cm^{-1} and between 1700 and 1500 cm^{-1}. UV-vis analysis shows that all films displayed an absorbance peak between 280 and 385 nm. These peaks are shifted toward higher wavelengths after irradiation This clearly showed some modifications in the interactions (hydrogen bonds, amide groups) between polymer chains induced by the irradiation.

1. Introduction

The waste generation increases with the population and the urbanization. Most of solid wastes (38%) come from plastic packaging (Duval, 2004). Consequently, the environmental impact of non-biodegradable plastic material wastes is a serious and major concern. Biodegradable films made from renewable biopolymers are a good alternative to produce environmental friendly packaging, thereby reducing plastic wastes (Hoque, Benjakul, & Prodpran, 2010; Tharanathan, 2003). In the last decade, there has been a marked increase in interest in the use of biodegradable materials for packaging, agriculture, medicine and other areas. Biodegradable polymeric films for packaging are of main attention (Akter et al., 2012) as they offer many advantages over synthetic or non-biodegradable polymers for film or coating applications on foodstuff. Films prepared from polysaccharides are reasonably resistant films but exhibit poor water vapor barrier due to their hydrophilic nature (Guilbert, 1986), whereas protein-based films show better mechanical and oxygen barrier properties (Khwaldia,

Abbreviations: CS, Chitosan; G, Gelatin; FFS, Film Forming Solution; EB, Electron beam; ESEM, Environmental Scanning Electron Microscopy; WVP, Water Vapour Permeability; RH, Relative Humidity; TS, Tensile Strength; YM, Young's Modulus; E, Elongation at break; FTIR, Fourier Transformed Infra Red; UV-vis, Ultra-violet visible; ESR, Electron Spin Resonance.

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Perez, Banon, Desobry, & Hardy, 2004), but are less effective barrier to gases (Nisperos-Carriedo, 1994). For that reason, film performances may be enhanced by producing composite and blend systems, where hydrocolloids (mixtures of proteins or/and polysaccharides) form a continuous and more consistent network (Porta, Mariello, Dipierro, Sorrentino, & Giosafatto, 2011). On the one hand, chitosan, a cationic polysaccharide obtained from the deacetylation of chitin, is currently used in a wide range of applications in the food, drug and pharmaceutical fields owing to its non-toxicity, biodegradability and biocompatibility (Fan et al., 2014). This polymer also displays an intrinsic as bacteriostatic and fungistatic activity (Dutta, Tripathi, Mehrotra, & Dutta, 2009; Shahidi & Arachchi, 1999). The term "cationic" polymer rises from the positive charge in acidic to neutral solution due to the protonation amino group (pKa value of around 6.5). On the other hand, gelatin, obtained by partial degradation of collagen has been one of the first polymers used for edible films (Rivero, García, & Pinotti, 2009). Gelatin is relatively low cost and displays noteworthy filmogenic properties (Arvanitoyannis, Psomiadou, Nakayama, Aiba, & Yamamoto, 1997; Cao, Fu, & He, 2007a; Eastoe & Leach, 1997). Gelatin has an isoelectric point between pH 5 and pH 9, depending upon the source and method of production. Chitosan and gelatin blend films have been shown to be homogenous due to the good miscibility between both biopolymers by electrostatic and hydrogen bonding when chitosan is positively charged and gelatin is negatively charged under appropriate conditions of pH and good choice of the initial polymer characteristic (example: percentage of deacetylation for chitosan, pI for gelatin …). This is particularly important to improve the final network properties as compared to those obtained from the pure polymers (Pereda, Ponce, Marcovich, Ruseckaite, & Martucci, 2011).

One of the promising ways to overcome the poor mechanical properties is to modify the physical properties of the films by inducing both intermolecular and intramolecular chemical bonding through chemical, enzymatic or physical means (Rhim, Wu, Weller, & Schnepf, 1999a). These treatments allow to modify the polymer network through the cross-linking of the polymer chains. Chemical treatments include the use of crosslinking agents such as glutaraldehyde in order to improve the functionalities of polysaccharide films (Mathew & Abraham, 2008). Cross-linking has also been used to improve the mechanical strength and barrier properties of protein films (Wihodo & Moraru, 2013). Chemical agents used for covalent cross-linking of proteins include among others glutaraldehyde, glyceraldehyde, formaldehyde and glyoxal (Hernandez-Munoz, Villalobos, & Chiralt, 2004; Orliac, Roully, Silvestre, & Rigal, 2002). However, most of these agents can often induce toxicity or lead to other undesirable effects. As they lose their edibility, the addition of such crosslinking agents in edible films packaging is obviously not recommended (Chambi & Grosso, 2006). Therefore, the possibility of using enzymatic methods to prepare polymeric films with good properties has been the object of recent extensive studies (Kumar, Bristow, Smith, & Payne, 2000). In previous works, it has been demonstrated that the enzymatic treatment with transglutaminase was efficient in lowering the WVP of gelatin films, but produced no change in the tensile strength of the modified film (Carvalho & Grosso, 2004). Porta et al. (2011) showed that chitosan and soy flour or whey proteins based films form a covalent crosslinking by using transglutaminase, with promising results to improve their mechanical resistance. Crosslinked proteins inside the network seem to reduce the intermolecular chain mobility of the proteins matrix. This consequently increases the tensile strength and reduces the extensibility of the modified films. But the high cost of some enzymes limits their use for further applications in the field of packaging (Cao, Fu, & He, 2007b). Thus other types of treatments had to be found in order to replace chemical and enzymatic ways of crosslinking. Physical methods including thermal, UV, γ and electron beam irradiation have been shown to be effective enough to crosslink proteins and polysaccharides and to improve both barrier and mechanical properties (Jo, Kang, Lee, Kwon, & Byun, 2005; Ryshkova et al., 2011; Wihodo & Moraru, 2013). Irradiation can provide a cost-lowering and environment-friendly alternative to change the physical, chemical and/or biological characteristics of a product (DeKerf, Mondelaers, Lahorte, Vervaet, & Remon, 2001). Irradiation treatment also requires limited sample preparation. Moreover, it is fast and does not require catalysts or any increase in temperature (Woods & Pikaev, 1994). The use of electron beam or γ radiation offers many advantages over the use of UV radiation like continuous operation, minimum time requirement and less atmospheric pollution than chemical methods (Ghoshal, Khan, Noor, & Khan, 2009). The irradiation of polymeric materials with ionizing radiation (γ and electron beam) leads to the formation of very reactive intermediates, such as free radicals, ions and excited states. These intermediates can follow several quick reaction pathways that results in disproportionation, hydrogen abstraction, arrangements and/or the formation of new bonds through the polymers chains (Chmielewski, Haji-Saeid, & Ahmed, 2005) which modified the final structure of the network. Lacroix et al. (2002) and Lee, Lee, and Song (2004) demonstrated that γ -irradiation induced crosslinking in casein and soy proteins by the aggregation of polypeptide chains, resulting in a film with enhanced water barrier and mechanical properties. The exposure of proteins to ionizing radiation can cause conformational changes, oxidations of amino acids, ruptures of covalent bonds (network degradation), formation of protein free radicals, recombination and polymerization reactions. This can be used to improve the structure and mechanical properties of protein films (Wihodo & Moraru, 2013). Ressouany, Vachon, and Lacroix (1998) demonstrated that maximum puncture strength was obtained for caseinate films at an irradiation dose of 64 kGy. Furthermore, Micard, Belamri, Morel, and Guilbert (2000) showed that γ-irradiated gluten films had increased tensile strength, and decreased elongation at 10 kGy, whereas higher radiation dose (20 and 40 kGy) reduced both the observed effect. Similarly, Lee, Lee, and Song (2005) working on gluten films, reported that water vapour permeability was reduced by 29% after irradiation. They also showed a 1.5 fold increase in the tensile strength (at 50 kGy) and a decrease in the elongation at break, proving a crosslinking process.

The majority of papers deals with improving the functional properties of the final film by cross linking ways. Then cohesion between the two polymers was mainly done by chemical agents (glutaraldehyde, glyceraldehyde, formaldehyde) or enzymatic pathways (transglutaminase). Very few studies considered irradiation technique considered as a solvent free and "green" process. Indeed, Wihodo and Moraru (2013) used UV treatments and Lacroix et al. (2002) and Lee et al. (2004) preferred gamma irradiation. The originality of this work is to use the electron beam for crosslinking of oppositely charged biopolymers in a similar way as used for instance for pigment or printing curing in packaging technology. Less than 5 papers have been found on the film-forming ability of such combinations of gelatin and chitosan and any of them considered electron beam irradiation. The present study aims to better display the effect of electron beam irradiation doses by analyzing the microstructural, mechanical, transfer barrier and structural properties of chitosan-fish gelatin-based edible films. Spectroscopic techniques (FTIR, UV-Vis) have been used to better identify the interactions and structural changes in the biopolymer network.