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Impact of electron beam irradiation on fish gelatin film properties

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ABSTRACT

The objective of this work was to display the effect of electron beam accelerator doses on properties of plasticized fish gelatin film. Electron spin resonance indicates free radical formation during irradiation, which might induce intermolecular cross-linking. Tensile strength for gelatin film significantly increases after irradiation (improved by 30% for 60 kGy). The vapour permeability is weakly affected by irradiation. Surface tension and its polar component increase significantly and are in accordance with the increase of wettability. So, irradiation may change the orientation of polar groups of gelatin at the film surface and crosslink the hydrophobic amino acids. No modification of the crystallinity of the film is observed. These findings suggest that if structure changes, it only occurs in the amorphous phase of the gelatin matrix. It is also observed that irradiation enhances the thermal stability of the gelatin film, by increasing the glass transition temperature and the degradation temperature.

1. Introduction

Synthetic polymer materials have been widely used in every field of human activity during the last century. Most of solid wastes (38 wt%) come from plastic packaging. Consequently, the environmental impact of non-biodegradable plastic polymers is a serious and major concern. In order to reduce pollution caused by traditional plastic films, biodegradable films which are made out of renewable resources have shown a promising potential. Currently, they represent less than 10% of the use of polymers as films. These biosourced polymers are usually obtained from (a) chemical synthesis of bio-derived monomers, such as polylactate; (b) polymers naturally produced by microorganisms, such as polyhydroxybutyrate; and/or (c) extracted from biomass like plants (starch, cellulose) or coproducts from food industries (gelatin, whey protein, chitosan). Among the biosourced polymer-based films, protein-based films offer good mechanical and gas barrier properties (Jo, Kang, Lee, Kwon, & Byun, 2005). Indeed, the specific structure of proteins and their ability to form strong intermolecular covalent, ionic and hydrogen bonds allow to easily create linkages and then cohesive networks.

Gelatin, a natural polymer also considered as a by-product of food industry has a great potential for edible/biodegradable film applications. The rising interest in putting by-products from the fish industry to good use is one of the reasons why the industrial production of fish gelatin has been growing in recent years (Gomez-Guillen et al., 2002). Moreover, socio-culturally, marine gelatins are regarded as an alternative to terrestrial mammalian (bovine and porcine) gelatins, since pork consumption is forbidden by Judaism and Islam religions. Fish gelatin is abundant, biodegradable, has excellent film-forming properties, good barrier against oxygen and aromas at low water content, and is of relatively low cost. As a rule, the physical properties of gelatin films depend chiefly on the properties of the raw materials extracted from the different animal species and on the processing conditions of gelatin manufacturing which affect physicochemical properties of film. Avena-Bustillos et al. (2006) reported the water vapour permeability (WVP) of cold-water fish-gelatin films to be significantly lower than that of films made from warm water fish gelatin or mammalian gelatin and explained the tendency of fish-gelatin films to exhibit lower WVP values than land animal-gelatin films in terms of the amino acid composition, since fish gelatins, especially cold-water fish gelatins, are known to contain higher amounts of hydrophobic amino acids and lower amounts of

Abbreviations: FFS, film forming solution; EB, electron beam; ESR, electron spin resonance; ESEM, environmental scanning electron microscopy; XRD, X-rays diffraction; DSC, differential scanning calorimetry; TGA, thermogravimetric analysis; WVP, water vapour permeability; RH, relative humidity; TS, tensile strength; *E*, elongation at break; Tg, glass transition temperature; γ_S, surface tension; γ_S^d, dispersive component of surface tension; γ_S^p, polar component of surface tension.

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hydroxyproline. Similarly, using equivalent procedures and plasticizing conditions (sorbitol or glycerol, 25 at 30% of gelatin content), the WVP of halibut-skin gelatin films (Carvalho et al., 2008) and tuna-skin gelatin films (Gomez-Guillen, Ihl, Bifani, Silva, & Montero, 2007) was also reported to be lower than that of mammalian-gelatin films (Sobral & Habitante, 2001). For this reason we have interested to use fish as source of gelatin based film. However, the main limitation of gelatin films lies in its high sensitivity to water and then it is necessary to improve the barrier and physical properties of this biopolymer. Various methods to enhance the physical properties of protein films have been considered. One of the most common solutions consist in blending gelatin with another polymer in order to improve the final network properties (BenBettaïeb, Kurek, Bornaz, & Debeaufort, 2014). The addition of hydrophobic substances can also enhance the gas barrier properties but depends if added as emulsion-based structures or as laminates (multilayer films). Indeed, Apostolov, Fakirov, Evstatiev, Hoffmann, and Friedrich (2002) showed substantial increases of Young's modulus and tensile strength in comparison to neat gelatin (not laminated) by a factor of 2–3 and 4–5, respectively, for both linen- and silk-reinforced gelatin laminates. This can be due to establishment of chemical links between the matrix and the reinforcing agent (silk and linen). In the same way, Martucci and Ruseckaite (2009) showed that the association of gelatin based layers subjected to different technological treatments such as cross-linking, compounding with clay and heat-compression moulding can provide a new multilayer material with modulated biodegradability under soil burial conditions. The same authors, Martucci and Ruseckaite (2010) founded that multilayer film derived from bovine gelatin film have lower water vapour permeability and total soluble matter but higher tensile strength and elastic modulus compared to the single layers. Another solution consists in making a bilayer structure with another polymer. Irissin-Mangata, Bauduin, and Boutevin (2000) found that bilayer polymer films from wheat gluten and UV-curable resins have reduced water vapour permeability by more than 50% compared to the monolayer film. Crosslinking of proteins is another solution that can lead to stiffer and less permeable films. Several studies have investigated the improvement of functional properties via cross-linking induced by heat and chemicals agents (Micard, Belamri, Morel, & Guilbert, 2000), or enzymes (Carvalho & Grosso, 2004). However, most of these agents are costly and may induce toxicity or lead to other undesirable effects. Physical treatment using high energy irradiation can provide a cost-lowering and environmentally alternatives to change the physical, chemical and/or biological characteristics of a product. Irradiation treatment also requires limited sample preparation. Moreover, it is fast and does not require any catalyst or temperature increase (Woods & Pikaev, 1994). The irradiation of polymeric materials with ionising radiation (essentially high frequency ultraviolet (UV), gamma and electron beam) can lead to the formation of very reactive intermediates, free radicals, ions and excited states. These intermediates follow several quick reaction pathways that result in disproportionation, hydrogen abstraction, arrangements and/or the formation of new bonds within polymer chains which therefore modifies the final structure of the network (Chmielewski, Haji-Saeid, & Ahmed, 2005). Ouattara, Canh, Vachona, Mateescu, and Lacroix (2002) displayed that gamma-irradiation produced free-standing cross-linked milk proteins and therefore improved water vapour permeability and chemical stability. Gamma-irradiation also induced a substantial increase of high molecular weight protein components in film forming solutions. Lacroix et al. (2002) and Lee, Lee, and Song (2005) demonstrated that γ-irradiation was effective in inducing 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 ionising radiation can cause conformational changes, oxidations of amino acids, ruptures of covalent bonds (biopolymer degradation), formation of protein free radicals, recombination or polymerization reactions. This process can thus improve the structural and mechanical properties of protein films. In the same way, Lee et al. (2005) reported that water vapour permeability of gluten films was reduced by 29% after irradiation. Jo et al. (2005) found that gamma irradiation is also effective to crosslink proteins and to improve both gas barrier and mechanical properties. Similar result was shown by Inamura et al. (2013) in the case of composite gelatin-nut shell fibre after a 40 kGy irradiation dose. They found that thermal stability was improved after electron beam irradiation by the formation of a denser network via arrangement of chains. From Bhat and Karim (2009), the crosslinking appears to dominate over the effect of chain degradation as manifested by the increase in gel strength after UV irradiated fish gelatin. More generally, most food proteins undergo irradiation-induced cross-linking, which can be used to subsequently improve the film functional properties.

Among the previously described irradiation processes, very few studies are related to the effect of electron beam technology on functional properties of packaging film derived from natural biosourced polymers. The present work focuses on the effect of electron beam irradiation on fish gelatin films. The main objectives are to assess the effects of the irradiation doses on moisture transfer and water wettability in relation with the structural and thermal properties of fish gelatin film.

2. Materials and methods

2.1. Materials and reagents

Commercial grade fish gelatin (Pharmaceutical Gelatin, Rousselot 200 FG 8, with a 180 Bloom degree, a viscosity of 4 mPa s and 5.4 pH at 45 °C) was used as the gelatin film-forming solution. Anhydrous glycerol (GLY) (Fluka Chemical, 98% purity, Germany) was used as plasticizer in order to improve the mechanical properties of the films. Potassium chloride (KCl, Sigma) and magnesium nitrate ($Mg(NO_3)_2$, Sigma) were used to prepare saturated salt solutions to fix the relative humidity for water vapour and gas permeability measurements.

2.2. Film preparation

A 6% (w/v) fish gelatin solution was prepared in distilled water under continuous stirring and heating at 70 °C during 30 min. Glycerol (10% w/w of polymer dry matter) was added to the film solution after dispersion of gelatin. pH of gelatin solution was adjusted to about 4.9. The film-forming solution was then poured into a plastic Petri dish (13.5 cm diameter). In order to produce the films, the solvent was removed by drying in a ventilated climatic chamber (KBF 240 Binder, ODIL, France) at 25 °C and 45% relative humidity (for 18–24 h depending on the volume of film-forming solution poured). After drying, the films were peeled off from the surface and stored up to equilibration in a ventilated climatic chamber (KBF 240 Binder, ODIL, and France) at 50% RH and 25 °C before each measurement.

2.3. Film irradiation

Radiation processing was carried out at the AERIAL pilot plant (Innovation Park, Illkirch, Strasbourg, France), using a linear electron accelerator at ambient temperature (20 ± 0.5 °C). Thin dried films (80–100 μm thickness) were irradiated with electron beam carrying 2.2 MeV energy and 0.3 kGy/s dose rate. The doses