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Cross-linking of fish gelatins to develop sustainable films with enhanced properties

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ABSTRACT

Transparent, homogenous and resistant renewable films were prepared in this work. In contrast to other natural cross-linkers, the addition of citric acid into film forming solutions caused no change in color, highlighting the potential of these cross-linked films for packaging applications, in which film appearance is a key factor for consumer acceptance. Furthermore, modified films showed lower gloss values, indicating the formation of a rougher surface, which would provide more convenient surface properties when printing the film for commercial purposes was intended. In addition, modified films showed improved light barrier properties, which highlight the potential of these films to prevent oxidation caused by light. Finally, the environmental assessment showed that composting as disposal scenario could provide environmental benefits when using these renewable films, although improvements in raw material extraction and film manufacture are still needed.

1. Introduction

The use of polymers derived from biomass, such as proteins [1] and polysaccharides [2,3], has grown in the last years, mainly due to their film forming ability, biocompatibility and biodegradability [4–6]. Among proteins, gelatin is the most widely used due to its abundance [7–10]. This biopolymer is obtained by the hydrolytic treatment of collagen, the major structural protein of most connective tissues [11–14]. Although further research has been performed in relation to mammalian gelatins, fish gelatin is actually preferred owing to vegetarianism concerns as well as the potential of halal and kosher markets [15]. In particular, fish gelatin is an inexpensive raw material extracted from abundant fish wastes, such as skin and bones from fish processing industries [16,17], which contain 27–49% protein on a dry weight basis [18]. Therefore, valorization of these wastes could facilitate waste management as well as promote the development of novel and more sustainable films [19–22]. Furthermore, since these films are biodegradable, they could be treated by composting after disposal, reducing environmental impacts associated to non-biodegradable plastic films [23].

In spite of the environmental benefits, contributing to the efficiency in the use of raw materials and the reduction of waste after disposal, the properties of fish gelatin-based materials need to be enhanced to produce competitive films for packaging applications, in which properties related to film appearance greatly affect the consumer decision to purchase.

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Specifically, physicochemical properties, such as solubility, transparency, color and gloss, are some of the main film attributes indicative of the commercial potential of the films developed. Additionally, other functional properties, such as tensile strength, flexibility, and water vapor permeability must be also assessed in order to predict the behavior and thus, the suitability of fish gelatin films. In general, biopolymeric films are brittle and hydrophilic [14], and so biopolymer modification is needed in order to enhance those functional properties and acquire the properties required for packaging applications [24–26].

Different approaches, such as blending of biopolymers, manufacture of multilayers and chemical cross-linking have been used to improve the functional properties of bio-based films. With regard to chemical cross-linking, aldehydes have been widely used to react with biopolymers. However, due to their toxicity [27–29], natural cross-linkers are preferred. In this work, citric acid was selected to cross-link fish gelatin. Citric acid is an aliphatic polyfunctional bio-based raw material that contains two reactive primary carboxylic groups, one sterically hindered hydroxyl group and one less reactive tertiary carboxylic group [30]. Recently, the use of citric acid as cross-linking agent for polysaccharides, such as starch [31] and pectin [32], has been reported; however, the available literature concerning the effect of citric acid in proteins is very limited. In this context, the aim of this work was to analyze the effect of citric acid content on optical, mechanical and barrier properties of fish gelatin films and relate the final properties achieved to the changes observed by the physicochemical analysis performed in this study. Furthermore, the environmental aspects involved in the manufacture of these renewable and biodegradable films were assessed by the carbon footprint analysis.

2. Experimental

2.1. Materials

Fish gelatin was purchased from Healan Ingredients (East Yorkshire, UK). Glycerol and citric acid (CA) were obtained from Panreac (Barcelona, Spain). All chemicals were used as received without further purification.

2.2. Preparation of films

Fish gelatin films were prepared by mixing gelatin and CA in distilled water. The acid contents employed in this work were 10, 20, 30 and 40 wt.% on gelatin basis. Solutions were heated at 80 °C for 30 min and stirred at 200 rpm. Then, 20 wt.% glycerol (on gelatin basis) was added as a plasticizer and solution pH was adjusted to pH 10 with NaOH (1 N). The heating procedure was repeated and finally, solutions were poured into Petri dishes and allowed to cool for 48 h at room temperature. Films were designated as 0CA, 10CA, 20CA, 30CA and 40CA, as a function of the citric acid content. The films prepared without CA (0CA) were used as control films. All films were conditioned in a controlled environment chamber at 25 °C and 50% relative humidity before testing.

2.3. Moisture content (MC) and total soluble matter (TSM)

Films were weighed (w_0) and then dried in an oven at 105 °C for 24 h. After this time, samples were reweighed (w_1) to determine their MC:

$$MC(\%) = \frac{w_0 - w_1}{w_0}\ 100$$

To obtain TSM values, the dried specimens were immersed in 200 mL of distilled water for 24 h. Afterwards, the films were dried in the oven at 105 °C for 24 h and weighed (w_2). TSM values were calculated by the following equation:

$$TSM(\%) = \frac{w_1 - w_2}{w_1} 100$$

2.4. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of films and pure components (fish gelatin, glycerol and CA) were carried out on a Nicolet 380 FTIR spectrometer using ATR Golden Gate. A total of 32 scans were performed at a resolution of 4 cm^{-1} in the wavenumber range from 800 to 4000 cm^{-1}.

2.5. Gloss measurement

Film gloss was determined using a Multi Gloss 268 Plus gloss meter. Gloss values were measured at 60° incidence angle, according to ASTM D523.