



Preparation and functional properties of fish gelatin–chitosan blend edible films

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ABSTRACT

With the goal of improving the physico-chemical performance of fish gelatin-based films, composite films were prepared with increasing concentrations of chitosan (Ch) (100G:0Ch, 80G:20Ch, 70G:30Ch, 60G:40Ch and 0G:100Ch, gelatin:Ch), and some of their main physical and functional properties were characterised. The results indicated that the addition of Ch caused significant increase ($p < 0.05$) in the tensile strength (TS) and elastic modulus, leading to stronger films as compared with gelatin film, but significantly ($p < 0.05$) decreased the elongation at break. Ch drastically reduced the water vapour permeability (WVP) and solubility of gelatin films, as this decline for the blend film with a 60:40 ratio has been of about 50% ($p < 0.05$). The light barrier measurements present low values of transparency at 600 nm of the gelatin–chitosan films, indicating that films are very transparent while they have excellent barrier properties against UV light. The structural properties investigated by FTIR and DSC showed a clear interaction between fish gelatin and Ch, forming a new material with enhanced mechanical properties.

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1. Introduction

The environmental impact of non-biodegradable plastic material wastes is of increasing global concern. There is an urgent need to develop renewable and environmentally friendly bio-based polymeric materials (Khwalidia, Arab-Tehrany, & Desobry, 2010). Edible bio-based films have been investigated for their abilities to avoid moisture loss or water absorption by the food matrix, oxygen penetration to the food material, aromas loss and solute transports (Dutta, Tripathi, Mehrotra, & Dutta, 2009). Gelatin one of the most studied biopolymers for its film-forming capacity and applicability as an outer covering to protect food against drying, light, and oxygen (Gómez-Guillén et al., 2009a).

Fish gelatin has gained importance in recent years as a result of the outbreak of bovine spongiform encephalopathy, and the banning of collagen from pig skin and bone in some regions for religious reasons. Furthermore, fish skin, which is a major byproduct of the fish-processing industry, causing waste and pollution, could provide a valuable source of gelatin (Badii & Howell, 2006). With the appropriate film forming properties and good barriers against oxygen and aromas at low and intermediate relative humidity, gelatin is suitable for production of biodegradable packaging materials, as reviewed by Gómez-Guillén et al. (2009b). However, gelatin has

relatively poor water barrier and mechanical properties, which is the main drawbacks of gelatin films for application as packaging material (Chiou et al., 2008). One of the effective strategies, allowing maintaining the biodegradability, is to elaborate biocomposites by association of fish gelatin with other biopolymers exhibiting film forming properties and derived from renewable resources.

Chitosan is a natural polymer obtained by deacetylation of chitin, and when compared with other polysaccharides, chitosan has several advantages such as biocompatibility, biodegradability and no toxicity, while also presenting functional properties as bacteriostatic and fungistatic (Dutta et al., 2009; Shahidi, Arachchi, & Jeon, 1999). Chitosan-based materials may be used as edible films or coatings due to their unique property of increased viscosity upon hydration. Furthermore, chitosan films are tough, long-lasting, flexible, and very difficult to tear (Jeon, Kamil, & Shahidi, 2002). Hence, due to these interesting properties such as excellent film-forming capacity and good barrier and mechanical properties, it's a suitable material for designing packaging structures (Aider, 2010; Martins, Cerqueira, & Vicente, 2012). Because of its properties such as bioactivity, high mechanical strength and moisture transfer generally lower than pure gelatin films, a combination of fish gelatin with chitosan as blend could produce biocomposites with novel properties (Kolodziejaska & Piotrowska, 2007; Sionkowska, Wisniewski, Skopinska, Kennedy, & Wess, 2004).

Although some studies dealing with gelatin and chitosan composites have been performed, there is no previous report on the

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effect of different proportions of these biopolymers in the form of composites on the physico-chemical properties of fish gelatin-based films. Moreover, most of these studies have been focused on bovine hide gelatin and research about composite films prepared from fish gelatin are limited (Pereda, Ponce, Marcovich, Ruseckaite, & Martucci, 2011; Rivero, García, & Pinotti, 2009). Fish gelatin (especially cold-water fish gelatins) film, exhibits lower water vapour permeability than bovine or porcine gelatin, and this attributed to increased hydrophobicity due to lower proline and hydroxyproline contents, as the hydroxyl group of hydroxyproline is normally available to form hydrogen bonds with water molecules (Avena-Bustillos et al., 2006). Therefore, fish gelatin is a good alternate to consider when dealing with composite edible films aimed at reducing water vapour transmission. Upon considering the best characteristics of fish gelatin and chitosan separately, we speculated that their combination would lead to better films than those formed by each individual material alone.

Hence, the objectives of the present work were to examine the effect of different ratios of fish gelatin/chitosan on the functional characteristics of blend films such as water vapour permeability (WVP), film solubility, transparency and mechanical properties. The characterisation of biocomposites by thermal analysis (DSC) and infrared spectroscopy (FTIR) was performed.

2. Materials and methods

2.1. Materials

Gelatin from cold water fish skin and chitosan (medium molecular weight, 75–85% deacetylated) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Glycerol (analytical grade) and acetic acid were purchased from Merck Chemicals Co. (Darmstadt, Germany).

2.2. Preparation of the films

The gelatin films were prepared according to the casting technique described by Gómez-Estaca, Gómez-Guillén, Fernández-Martín, and Montero (2011) with slight modifications. Five groups of composite films with different ratios of gelatin to chitosan (100G:0Ch, 80G:20Ch, 70G:30Ch, 60G:40Ch and 0G:100Ch) were prepared. Single gelatin film forming solution (4%, w/v) was prepared by dissolving 4 g gelatin in 100 ml distilled water for 30 min and then heated at 45 °C for 30 min under continuous stirring. Ch solution was prepared with 1.5% (w/v) Ch in 1% (v/v) acetic acid, stirred overnight at room temperature, and filtered through a micron wire mesh to remove impurities.

The gelatin–Ch film forming solutions were prepared by mixing a 6%, 4% and 2% fish-skin gelatin solution with a 1.5% solution of Ch, in a proportion of 1:1 (v/v), to obtain a film-forming solution with different proportions, respectively (solutions 80G:20Ch, 70G:30Ch and 60G:40Ch). All mixtures were warmed and stirred at 45 °C for 30 min to obtain a good blend. Glycerol (0.3 g/g gelatin or Ch or gelatin plus Ch) was added as a plasticiser and solutions were again warmed and stirred at 45 °C for 15 min. The filmogenic solutions were degassed under vacuum for 15 min to remove air bubbles. Then, aliquots of 50 g of film-forming solutions were poured in polystyrene petri dishes (14 cm of diameter) and dried at ambient temperature (23–25 °C) for 72 h to yield a uniform thickness of $90 \mu\text{m} \pm 12$ in all cases except the 0G:100Ch formulations, which was $80 \mu\text{m} \pm 7$ thick. Thickness of films was determined using a micrometer (Mitutoyo Manufacturing Co. Ltd., Tokyo, Japan) to the nearest 0.001 mm at 9 random positions around the film, and average values were used in calculations. Films were conditioned at 25 °C and a relative humidity (RH) of $50 \pm 4\%$ RH for 48 h for further analysis.

2.3. Characterisation of the films

2.3.1. Mechanical properties

A universal testing machine (SMT-20, Santam, Tehran, Iran) equipped with a 60 N load-cell was used to measure tensile strength (TS), elongation at break (EAB%) and elastic modulus (EM) according to the ASTM standard method D 882-09 (2009). films strips of 110×20 mm were conditioned at 23 ± 2 °C and $53 \pm 2\%$ relative humidity for 48 h in an environmental chamber before testing. Initial grip separation and mechanical crosshead speed were set at 50 mm and 5 mm/min, respectively. Each type of film was tested by at least five replicates.

2.3.2. Water vapour permeability

The water vapour permeability (WVP) of films was measured gravimetrically according to the ASTM E96-05 method (2005) and adapted to hydrophilic edible films by McHugh, Avena-Bustillos, and Krochta (1993). Circular test cups were made of glass with 49 mm internal diameter and 1.1 cm height. Films without pinholes or any defects were sealed to the cup mouth containing 6 ml distilled water (100% RH; 2.337×10^3 Pa vapour pressure at 20 °C), placed in a desiccators at 20 °C and 0% RH (0 Pa water vapour pressure) containing silica gel. The water transferred through the film and adsorbed by the desiccant was determined from the weight loss of the permeation cell. The films were allowed to equilibrate for 2 h before the cells were initially weighed. The cells were weighted at intervals of 2 h during 10 h with an analytical balance (± 0.0001 g). The slope of weight loss versus time was obtained by a linear regression ($r^2 \geq 0.99$). The measured WVP of the films was determined as follows:

$$\text{WVP} = \frac{\text{WVTR} \times L}{\Delta P}$$

where WVTR is the water vapour transmission rate ($\text{g mm} / \text{kPa h m}^2$) through a film, calculated from the slope of the straight line divided by the exposed film area (m^2), L is the mean film thickness (mm), and ΔP is the partial water vapour pressure difference (kPa) across the two sides of the film. Three replicates of each film were tested.

2.3.3. Water solubility

Water solubility of the films was carried out according to the method of Contard, Guilbert, and Cuq (1992). Three pieces ($1 \times 4 \text{ cm}^2$) of film were weighed (± 0.0001 g) and subsequently dried in an air-circulating oven at 105 °C for 24 h. After this time films were recovered and re-weighed (± 0.0001 g) to determine their initial dry weight (W_i). Afterwards, the samples were immersed in 30 ml of distilled water and the system gently shaken (100 rpm) for 24 h at room temperature (22–25 °C). The samples were then passed through a filter paper (Whatman 1). Then the filter paper together with unsolubilised fraction was dried in a forced-air oven (105 °C, 24 h) and weighed (W_f). The film solubility (FS%) was calculated using the following equation:

$$\text{FS\%} = \frac{W_i - W_f}{W_i} \times 100$$

W_i = initial dry film weight; W_f = final dry film weight.

2.3.4. Light transmission and transparency

The barrier properties of films against ultraviolet (UV) and visible light were measured at selected wavelength between 200 and 800 nm using the method described by Fang, Tung, Britt, Yada, and Dalglish (2002). Film portions of 10×40 mm were placed into the test cell of a UV-1650 spectrophotometer (Model PC, Shimadzu, Kyoto, Japan), using an empty test cell as the reference. The measurement was done in triplicate and the average of three spectra

was calculated. The transparency of the films was calculated by the following equation:

$$\text{Transparency}(A/\text{mm}) = -\log T/x$$

where A = absorbance at each wavelength, T = transmittance (%) at each wavelength, x = film thickness (mm). According to the equation, high transparency indicates opaque.

2.3.5. Differential scanning calorimetry (DSC) analysis

Thermal properties of films were determined using a differential scanning calorimeter (DSC, Model 200-F3 Maia, Netzsch, Germany). Before analysis, films were conditioned in a desiccator containing dried silica gel for 2 weeks at room temperature (23–25 °C) to obtain dehydrated films. Aliquots of approximately 10 mg predried samples were placed into aluminium pans, sealed and scanned over the range of –50 to 150 °C with a heating rate of 10 °C/min. The empty aluminium pan was used as a reference.

2.3.6. Fourier-transform-infrared spectroscopy (FTIR)

The film samples were dried in a desiccator containing silica gel for 2 weeks before analysis. Pieces of film 2 cm in diameter were sandwiched between two KBr disks. FTIR spectra were recorded from wave number 400–4000 cm^{-1} in a Bruker Equinox 55 spectrometer (Bruker Banner Lane, Coventry, Germany). The spectra obtained were used to determine the interactions between fish gelatin and chitosan. For each spectrum, 16 scans were co-added.

2.3.7. Statistical analysis

The statistical analyses of the data were performed using analysis of variance (ANOVA) and the differences between means were evaluated by least significant difference multiple range test at $p \leq 0.05$. SPSS statistic program (SPSS 17.0 for window, SPSS Inc., Chicago, IL, USA) was used for data analysis.

3. Results and discussion

3.1. Edible films mechanical properties

Adequate mechanical strength and extensibility are generally required for a packaging film to withstand external stress and maintain its integrity as well as barrier properties during applications in packaging (Rao, Kanatt, Chawla, & Sharma, 2010). Blends of proteins with different ratios of polysaccharides can be useful to improve tensile properties. Representative stress–strain curves of the films are shown in Fig. 1. These curves exhibited the typical deformation behaviour; at low strains (<10%) the stress increased

rapidly with an increase in the strain and the slopes were in the elastic region defining the elastic modulus. At strains >10%, the stress increased slowly until failure occurred. Curves showed that gelatin film more flexible but brittle than Ch one, while blending enhanced the stiff and extensively compared with the parent films.

Table 1 shows the tensile strength (TS), percentage of elongation at break (% EAB) and elastic modulus (EM) of films equilibrated at 50% RH and 25 °C. Single gelatin films exhibited average tensile strength (TS) and elongation at break (EAB) values of 2.17 ± 0.97 MPa and $82.64 \pm 20.11\%$, respectively, being in the same range than those reported for other authors (Denavi et al., 2009; Limpisophon, Tanaka, & Osako, 2010). Conversely, Ch film showed substantially higher ($p < 0.05$) TS value (28.12 ± 6.01 MPa) and a reduced EAB% of 23.63 ± 8.37 , when comparing with gelatin film. These values are higher than those reported by Pereda, Amica, and Marcovich (2012) (TS = 8.41 MPa and EAB = 19.55%). As presented in Table 1, in composite films, the addition of Ch induced significant increased in the tensile strength, leading to stronger films as compared with gelatin film, but significantly ($p < 0.05$) decreased the elongation at break. A similar behaviour was observed by Gómez-Estaca et al. (2011), who studied composite films manufacture from tuna-skin or bovine hide gelatin and Ch (DD 85%). In the study of Pereda et al. (2011), tensile strength values reported for composite films based on bovine gelatin and chitosan were markedly reduced when comparing with control chitosan film, to the contrary of what occurred in the present study.

Elastic modulus, a measure of intrinsic film stiffness, is the slope of the linear range of the stress–strain plot (Mauer, Smith, & Labuza, 2000). Control Ch film (0G:100Ch) showed the highest in elastic modulus (1036.6 MPa). Elastic modulus (EM) significantly increased with incorporation of Ch in blend films (Table 1). Values obtained in this study showed that the ratio 60G:40Ch might be an optimum level of interactions between these biopolymers. Pranoto, Lee, and Park (2007) reported that there was an optimum level for interaction between polysaccharides and gelatin where gelatin was the major and dominant phase in the film system they used, and concluded that 2% was found to be beyond the optimum level of interaction between polysaccharides and gelatin. Thus, concluded that the strength and flexibility of the composite films could be modified by changing the ratio of protein to polysaccharides. However, we believe that the addition of Ch to gelatin films produced more flexible films suggests that Ch takes part in the weakening or reduction of the number of hydrogen bonds, acting as a plasticiser.

3.2. Water vapour permeability (WVP)

Since a main function of a food packaging is often to avoid or at least to decrease moisture transfer between the food and the surrounding atmosphere, or between two components of a heterogeneous food product, WVP should be as low as possible (Contard et al., 1992).

As shown in Table 1, Ch films exhibited better water vapour barrier properties than gelatin ones (0.367 vs. 0.826 g mm/kPa h m^2). Gelatin films with a higher amount of protein and thickness could adsorb more water from the environment, due to the presence of a wide range of hydrophilic amino acids in the gelatin (McHugh et al., 1993). Water vapour permeability of both biopolymers has been previously studied by other authors. Values for gelatin were comparable with those reported for cold-water fish gelatin films (Chiou et al., 2008) (0.857 g mm/kPa h m^2). The low WVP of fish skin gelatin films is related to their high hydrophobicity due to the reduced amount of proline and hydroxyproline compared to the mammalian gelatins.

The WVP of gelatin films were significantly reduced when Ch was added (Table 1), as this decline for the composite film with a

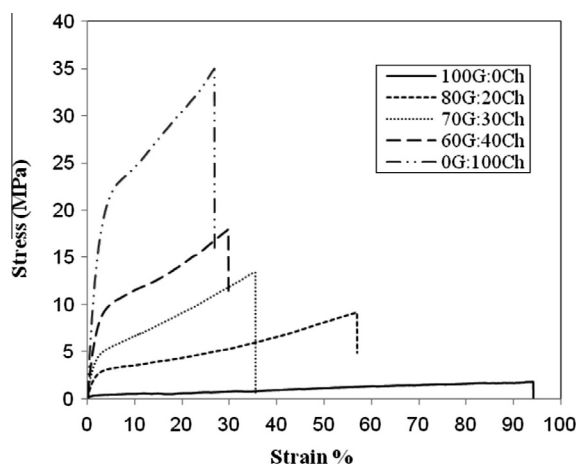


Fig. 1. Typical stress–strain curves of control (G and Ch) and their composites (80G:20Ch, 70G:30Ch and 60G:40Ch).

Table 1

Tensile strength (TS), elongation at break (EAB), elastic modulus (EM), film solubility and water vapour permeability (WVP) of films obtained with different gelatin-chitosan ratios.

Film	TS (MPa)	EAB (%)	EM (MPa)	Film solubility (%)	WVP (g mm/kPa h m ²)
100G:0Ch	2.17 ± 0.97 ^a	82.6 ± 20.1 ^a	92.2 ± 30.2 ^a	63.81 ± 1.78 ^a	0.826 ± 0.047 ^a
80G:20Ch	7.35 ± 3.45 ^b	66.6 ± 13.5 ^{ab}	234.2 ± 60.7 ^{ab}	39.09 ± 1.16 ^b	0.707 ± 0.052 ^b
70G:30Ch	13.08 ± 2.84 ^c	44.5 ± 17.8 ^c	439.3 ± 50.9 ^c	35.58 ± 1.00 ^c	0.602 ± 0.034 ^c
60G:40Ch	16.60 ± 1.19 ^{cd}	25.3 ± 5.0 ^{cd}	873.9 ± 58.0 ^{de}	29.96 ± 0.62 ^d	0.410 ± 0.034 ^d
0G:100Ch	28.12 ± 6.01 ^e	23.6 ± 8.3 ^{ce}	1036 ± 195.7 ^e	35.55 ± 0.27 ^{ce}	0.367 ± 0.004 ^{cd}

Reported values for each film are means ± standard deviation. Values means followed by the same letter are not significantly ($p > 0.05$) different according LSD test.

60G:40Ch ratio has been of about 50% ($p < 0.05$). This could be explained considering that chitosan might enhance the cross-linking of gelatin and decrease the free volume of the polymeric matrix, thus decreasing the diffusion rate of water molecules through the films, resulting in the lower WVP of the films (Cao, Fu, & He, 2007). Kolodziejaska & Piotrowska (2007) found decreased WVP of cod skin gelatin based edible films when chitosan was added. These authors represented that neither the gelatin and the chitosan pure films nor the compound ones were significantly different. Similar results were also observed by Pereda et al. (2011) in films based on bovine hide gelatin and chitosan, but there was no statistical difference in WVP between chitosan–gelatin film and gelatin control one.

3.3. Water solubility

As can be seen in Table 1 the water solubility of gelatin films is relatively high around 64%, that was in accordance with the values reported by Jiang, Liu, Du, and Wang (2010) for films elaborated from catfish skin gelatin and were considerably lower than those reported for cod skin gelatin films of around 25% (Denavi et al., 2009). The addition of Ch drastically improved the water resistance of fish gelatin films in the mixtures (80G:20Ch, 70G:30Ch and 60G:40Ch), with pronounced changes produced from the 60G:40Ch ratio onwards (around 30%), indicate an Ch proportion of 40% to be the optimum proportion for producing substantial physical interference in the entanglement of gelatin polypeptide chains within the film matrix. Such interference, which might have led to a significant blockade of gelatin ability to interact with water molecules, would be a main responsible for reducing the water solubility in the composite films. The obtained values did not respond to a simple rule of mixture and could result from interactions between both biopolymers caused by electrostatic forces, hydrogen bonding, etc. It has been reported that a polyelectrolyte positively charged (i.e. chitosan), and a polyampholyte negatively charged at the operating pH value (i.e. gelatin), can undergo associative interactions to form soluble polyelectrolyte complex (PEC) (Pereda et al., 2011). Reduction in water solubility due to blending with chitosan was already reported in the literature. Pereda et al. (2011) found a reduction of about 75% in water solubility of plasticised bovine hide gelatin film as a result of chitosan addition.

3.4. Light transmission and transparency

Optical properties are essential to define the ability of films and coatings to be applied over a food surface, since these affect the appearance of the coated product, which is an important quality factor (Pereda et al., 2012). Light transmission and transparency of all films at selected wavelengths are shown in Table 2. In the UV range of 200–280 nm, gelatin and blend films exhibited excellent UV barrier properties, which cause oxidative deterioration of packaged foods, leading to nutrient losses, discoloration and off-flavors (Martins et al., 2012). This result is in agreement with previous reports on gelatin-based films (Jiang et al., 2010). They both indicate that protein-based films are considered to have high UV barrier properties, owing to their high content of aromatic amino acids which absorb UV light. Light transmission of Ch films was negligible at 200 nm, but was relatively high at 280 nm (54.7%).

As shown in Table 2, the transmission of visible light was greater than 80% at 400–600 nm and greater than 90% at 800 nm for all films, while transparency was less than 1 at 600 nm. The results indicated that gelatin–chitosan films were very transparent (lower in transparency value). Gelatin film transparency was 0.56 A600/mm. The obtained values were lower than those reported by Rivero et al. (2009) and Pereda et al. (2011) for bovine-gelatin films (0.68 and 0.97, respectively) and some commonly used synthetic films such as low-density polyethylene (3.05 A600/mm) and oriented polypropylene (1.67 A600/mm). These findings are important since film opacity is a critical property that conditioned film applications, particularly if the film will be used as a surface food coating or for improving product appearance. The addition of Ch to gelatin films led to increased transparency values and therefore opacity of the films. Transparency values of blend films did not differ markedly from that of gelatin control film (Table 2), being therefore transparent.

3.5. Thermal properties

The DSC thermograms of the films with different fish gelatin–Ch mass ratios are shown in Fig. 2. Single fish gelatin film had T_g of 29.8 °C, which is higher than those of films made from tuna skin gelatin (T_g , 7.4 °C) (Gómez-Estaca et al., 2011), but was lower than T_g values reported for unplasticised cod gelatin films (T_g , 99 °C) (Staroszczyk, Pielichowska, Sztuka, Stangret, & Kolodziejaska,

Table 2

Light transmission (%) and transparency of films obtained with different ratios of fish gelatin (G) and chitosan (Ch).

Samples	Light transmission at different wavelengths (%)							Transparency
	200	280	350	400	500	600	800	
100G:0Ch	0.28	6.32	67.60	82.03	87.70	89.74	90.36	0.56
80G:20Ch	0.21	9.37	69.18	82.98	88.92	90.15	90.99	0.58
70G:30Ch	0.08	18.36	73.62	84.33	89.33	90.15	90.99	0.61
60G:40Ch	0.18	27.66	74.81	85.11	89.53	90.36	90.99	0.76
0G:100Ch	0.30	54.70	73.45	84.72	88.92	89.94	90.57	0.95

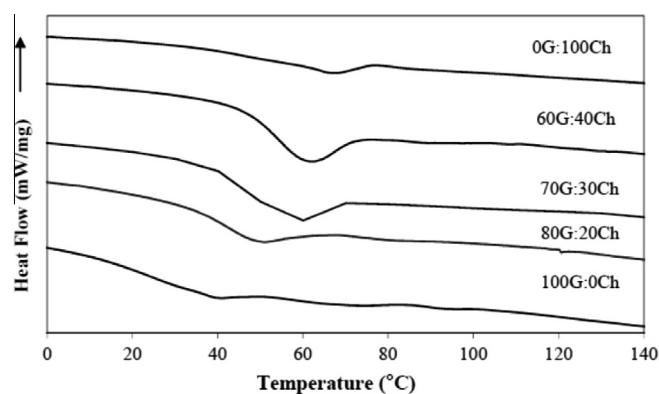


Fig. 2. DSC thermograms of films with different fish gelatin:chitosan ratios.

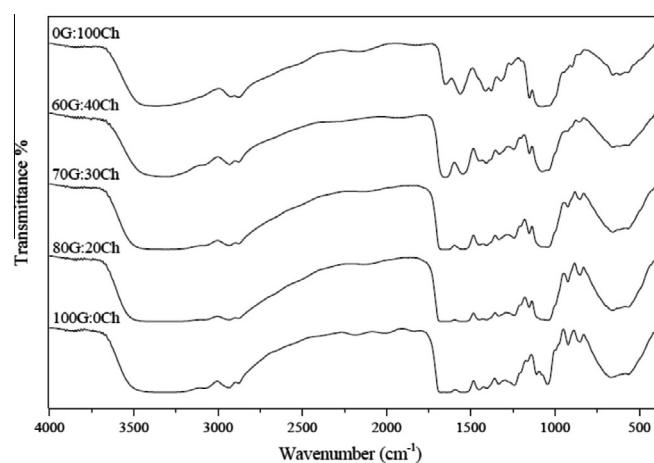


Fig. 3. FTIR spectra of films with different fish gelatin:chitosan ratios.

2012). Su, Huang, Yuan, Wang, & Li (2010) concluded that plasticizers like glycerol reduce T_g values when incorporated into carboxymethyl cellulose and soy protein isolate films, probably due to the ability of glycerol to penetrate between the polymer chains and therefore weaken the interaction between polysaccharides and proteins. On the other hand, T_g values reported for the plasticised films made from bovine-hide gelatin (Gómez-Estaca, Montero, Fernández-Martín, Alemán, & Gómez-Guillén, 2009) was 41.5 °C.

In the blend films with increasing the Ch content, T_g of gelatin film gradually increased and reached 55.9 °C at 60G:40Ch ratio. An increase of T_g of gelatin in the blend film might be assigned to the intermolecular interaction between G and Ch. It is well known that the T_g is an important criterion for the miscibility of the components. In a completely miscible blend of two polymers, only one T_g is observed in DSC thermograms (Suyatma, Copinet, Tighzert, & Coma, 2004). In the present study, the fish gelatin–Ch films show one T_g (45–55.9 °C) value that is different to that of the pure gelatin film (29.8 °C) and the Ch film (56.1 °C), indicating that gelatin and Ch have good miscibility and form a wide range of blends where new hydrogen bonding networks appear (Sionkowska et al., 2004).

3.6. FTIR spectroscopy of films

Fig. 3 shows FTIR spectra of gelatin, Ch and blend films. The spectra of gelatin film (control) showed characteristic bands at approximately 3320 cm^{-1} (amide-A, NH-stretching), 1677 cm^{-1} (amide-I, C=O stretching), and 1242 cm^{-1} (amide-III, C–N and

N–H stretching), (Pranoto et al., 2007; Staroszczyk et al., 2012). The main characteristic absorption bands of the Ch film at 1651, 1563 and 1411 cm^{-1} are assigned to the amide I, amide II and O–H bending, respectively. The assignment of these absorption bands are in agreement with those reported for Ch films (Abugoch, Tapia, Villamán, Yazdani-Pedram, & Díaz-Dosque, 2011). The spectra of the blend films exhibited the characteristic peaks of gelatin and Ch in proportion to the ratio between both components, with a slight difference in the region ranging from 1680 to 1630 cm^{-1} . With respect to gelatin-containing films, changes within this frequency range are indicative of alterations in collagen or gelatin secondary structure involving the amide-I region (Muyonga, Cole, & Duodu, 2004). Ch addition caused conformational changes in gelatin polypeptide chains resulting in a decrease in the presence of single α -helices, random coils and disordered structures, as evidenced by peak decreases at $\sim 1662 \text{ cm}^{-1}$ and $\sim 1644\text{--}1654 \text{ cm}^{-1}$ (Prystupa & Donald, 1996). This effect was most pronounced in the 60G:40Ch mixture, reaching intermediate values in mixtures 80G:20Ch and 70G:30Ch. The absorbance of amide-II and amide-III bands increases slightly with increasing Ch ratio, which might be related to amino and carbonyl moieties, evidenced that these groups interact mainly through electrostatic interactions, confirming the formation of a soluble PEC. The formation of gelatin–Ch PECs has been reported by other authors (Pereda et al., 2011; Rivero et al., 2009; Sionkowska et al., 2004).

4. Conclusions

In this study, improvement of fish gelatin film properties was investigated by Ch association. Fish gelatin and Ch were totally compatible to form solutions and films. The addition of these negatively charged polysaccharides could improve the properties of films made from fish gelatin by improvement mechanical properties and decreasing permeability. Hence, it is possible to replace mammalian gelatin in some applications. Moreover, the concentration of the two biopolymers in the film affected the physical, mechanical and optical properties of the films to various extents. In this case, The film prepared with the blend 60G:40Ch was found to be the best as it had lower water vapour permeability and film solubility. These results suggest a high potential of these films to be used as active packaging materials, and further studies would be required to determine the use of these films in commercial food systems.

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