Polymer blending effects on the physicochemical and structural features of the chitosan/poly(vinyl alcohol)/fish gelatin ternary biodegradable films

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Abstract

Films with appropriate mechanical properties and low permeability are very important for food packages. The aim of this research was to develop and characterize the ternary films made from chitosan (CH), poly(vinyl alcohol) (PVA), and fish gelatin (FG) at different blend compositions (50/50/0, 40/40/20, 35/35/30, 30/30/40, and 25/25/50, CH/PVA/FG) *via* a simple casting method. Stress-strain curves showed that the incorporation of 20% FG into the films made them tougher as well as making them more elastic; optimum ternary films were obtained using CH/PVA/FG ratio of 40/40/20, giving maximum values of TS and EAB as 41.93 ± 3.24 MPa and $133.13 \pm 13.23\%$, respectively. The water vapor permeability (WVP) values of the ternary films were in the range of 0.686-0.818 g mm/kPa h m². With increasing FG content, the WVP of the films increased to some extent, whereas the water solubility was reduced up to 23%. Water absorption increased with increasing FG concentration up to 874%. Meanwhile, the ultraviolet-visible-light barrier of the resultant ternary films was significantly improved with the addition of FG; at the same time, an increase in FG concentrations also made the films more opaque and improved their thermal stability. FT-IR spectra showed interactions through hydrogen bonding between the polar groups of FG and hydroxyl moieties of CH and PVA in the blends, which enhanced the compatibility between the three polymers. X-ray diffraction analysis suggested compatibility among the polymeric-blends, and changes of the surface of the films was confirmed by SEM and AFM analyses. The obtained results suggested the effectiveness of blending approach in improving the compatibility of polymers and overall functionality of films.

Keywords: Chitosan, Poly(vinyl alcohol), Fish gelatin, Ternary biodegradable films, Packaging materials

1. Introduction

Global bioplastics market will be of worth US\$ 43.867 billion in 2022, growing from US\$ 17.015 billion in 2017, at a CAGR (Compound Annual Growth Rate) of 20.85% over the forecast period (Global Bioplastics Market - Forecasts from 2017 to 2022). This emphasizes the fast development in application and production of bio-based materials in packaging which is in line with government regulations for green procurement policies. Regarding this, the exploration of new bio-based packaging materials like edible and biodegradable films has increased (Desobry & Debeaufort, 2011; Kaur, Jindal, Maiti, & Mahajan, 2019).

Fish gelatin (FG), major by-product of the fish-processing industry, is an encouraging alternative for mammalian-based (porcine and bovine) gelatin, since it doesn't have any safety issue and it has lower gel strength, melting temperature and water vapor permeability which are due to the lower levels of proline and hydroxyproline (de la Caba et al., 2019; Hosseini & Gómez-Guillén, 2018). However, FG-based films have high water solubility and relatively weak mechanical properties such as low tensile strength which can be improved by blending with other biodegradable polymers (Gómez-Guillén, Giménez, López-Caballero, & Montero, 2011). The blending of two oppositely charged biopolymers has been shown to lead to completely different physical and mechanical attributes of the resulting composite films compared to those of the starting materials (Wang et al., 2018). Chitosan (CH), a cationic polysaccharide, is a very promising biopolymer because it is environmentally friendly, non-toxic, odorless, biofunctional, chemically functionalizable, and low-permeable to oxygen (Kanatt, Rao, Chawla, & Sharma, 2012).

Nowadays, the blending of natural and synthetic polymers has gradually become an innovative approach to improve the cost-performance ratio of the resulting films. Poly(vinyl alcohol)

(PVA) is an attractive synthetic polymer suitable for mixing with biopolymers to improve the functional characteristics because of its interesting physical properties, which arise from the presence of O-H groups and the hydrogen bond formation (Bonilla, Fortunati, Atarés, Chiralt, & Kenny, 2014). In addition, it is easily soluble in water, biodegradable, and it has excellent chemical resistance and good mechanical properties; because of its suitable film-forming capabilities, PVA is used as an ingredient in food and pharmaceutical applications, for example, in the production of coatings and films (Giteru, Ali, & Oeya, 2019). Since FG, CH, and PVA have many advantages, these three components are widely used in the preparation of packaging materials, thereby generating a large amount of reference data on new composite materials; however, to the best of our knowledge, studies on combinations of the three polymers have not been reported yet.

The objective of this study was to evaluate the effect of different CH/PVA/FG blending ratio on the most relevant characteristics of the resultant films including mechanical and physical (water vapor permeability (WVP), solubility, swelling, water contact angle (WCA), color, and light-barrier properties) attributes. Furthermore, in order to determine the structural characterization of the films, Fourier-transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and atomic force microscopy (AFM) measurements were also taken.

2. Materials and methods

2.1. Materials

Cold water fish skin gelatin (FG), chitosan (CH) (medium molecular weight, 75-85% degree of deacetylation), and poly(vinyl alcohol) (PVA) (MW: 89000-98000, degree of hydrolysis: 99%)

were purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetic acid and glycerol were purchased from Merck Chemicals Co. (Darmstadt, Germany).

2.2. Preparation of CH/PVA/FG ternary films

The preparation process for the ternary films is shown in Fig. 1. A series of CH/PVA/FG ternary blends (50CH/50PVA/0FG), (40CH/40PVA/20FG), (35CH/35PVA/30FG), (30CH/30PVA/40FG) and (25CH/25PVA/50FG) were processed into films by a casting method through varying the FG concentration from 0 to 50%. CH/PVA binary blend film which is considered as the control film was prepared in a typical procedure as reported by Bonilla et al. (2014) with slight modifications. CH film-forming solution (FFS) (1.5% w/v) was prepared with 1.5 g CH in 1% acetic acid, stirred overnight at room temperature. Meanwhile, PVA solution (2% w/v) was prepared by dissolving 2 g PVA in 100 mL distilled water under magnetic stirring at 85 °C for 2 h. Then, CH and PVA solutions were blended together to form a homogeneous CH/PVA blend solution. FG film solution was prepared according to the method described by Hosseini, Rezaei, Zandi, and Farahmand Ghavi (2013) with some modifications. The FG solution (2% w/v) was prepared by dissolving 2 g gelatin in 100 mL of distilled water for 30 min and then heated at 45 °C for 45 min under continuous stirring.

In order to prepare ternary blend films, defined ratios of FG as mentioned above were gradually replaced with CH/PVA up to 50%. All mixtures were warmed and stirred at 45 °C for 30 min to obtain a good blend. Then, glycerol (0.3 g/g dry matter) was added as a plasticizer and solutions were again heated for 15 min at 45 °C. In order to provide a uniform thickness of 48 ± 4 μ m in all film samples, the total solids content was kept at approximately 0.27 g. Finally, the FFSs were degassed under vacuum for 15 min to remove air bubbles; after degassing, aliquots of 15 mL of FFSs were poured into polystyrene petri dishes (8 cm of diameter) and dried in an oven at 40 °C

for 48 h. The dried films were peeled off and stored at 25 °C with 50 ± 4% RH for 48 h until further analysis.

2.3. Characterization of the ternary films

2.3.1. Film thickness

A digital micrometer (Mitutoyo Manufacturing Co. Ltd., Tokyo, Japan) was applied to measure the film's thickness to the nearest 0.001 mm at 9 random positions around the film, and average values were used in calculations.

2.3.2. Tensile testing

Tensile properties were determined using a universal testing machine (TVT-300Xp, TexVol Instruments, Viken, Sweden) according to ASTM standard method D 882-09 (ASTM, 2009) with the adaptations proposed by Zhang et al. (2019). Film specimens (rectangular strips of 60 × 10 mm) were conditioned at 23 ± 2 °C and 53 ± 2% RH for 48 h in an environmental chamber before testing. The test conditions included; a load cell of 50 N, a cross-head speed of 1 mm/min, and an initial separation of the grips 30 mm. The tensile strength (TS) and elongation-at-break (EAB) were determined from the stress-strain curves, estimated from force-distance data. At least five film samples were tested for each treatment.

2.3.3. Determination of water vapor permeability (WVP)

The WVP was determined following a standard method (ASTM E96-05) (ASTM, 2005). The circular glass cups used for testing had a diameter of 49 mm and a depth of 1.1 cm. Films without defects were cut and attached to the cup mouth containing 6 mL of distilled water, and the edges of the samples were sealed thoroughly. Then, the cups were placed in a desiccator at

20 °C and 0% RH containing silica gel. Six readings were taken at a 2-h interval for 12 h and the weight difference was plotted in a scatter plot ($R^2=0.99$). The WVP was calculated according to Eq. (1).

(1)

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

where WVTR is the water vapor transmission rate (g mm/kPa h m^2) calculated from the slope of the straight line divided by the exposed film area (m^2), L is average film thickness (mm), and ΔP is the partial water vapor pressure difference (kPa) through two sides of the film.

2.3.4. Film solubility

Solubility studies of the ternary films were measured by adapting the method developed by Gontard, Guilbert, and Cuq (1992). Each film was cut into 1×4 cm dimensions, weighed and dried in a forced-air oven at 105 °C for 24 h; subsequently, films were regained and re-weighed to calculate their initial dry weight (W_i). They were then soaked in 30 mL of distilled water and mildly shaken (100 rpm, 24 h) at ambient temperature. The samples were filtered using Whatman No. 1; the filter papers plus undissolved portions were dried in an oven at 105 °C and weighed (W_f). The film solubility (FS%) was calculated using Eq. (2):

$$FS\% = \frac{W_i - W_f}{W_i} \times 100 \quad (2)$$

W_i = initial dry film weight (g), W_f = final dry film weight (g)

2.3.5. Film swelling

Film swelling attribute was determined according to the method reported by Hosseini, Javidi, and Rezaei (2016). Swelling kinetic was evaluated by immersing pre-weighed dry films (W_d) of

150 2 × 2 cm into 25 mL of distilled water at 30 °C under shaking. The weight gain of swollen film
 151 (W_s) was measured after 2 h, after gently blotting the surface with filter paper, until equilibrium
 152 was reached. The swelling ratio (SR%) was calculated according to Eq. (3):

$$SR\% = \frac{W_s - W_d}{W_d} \times 100 \quad (3)$$

153 Where W_s is the weight of swollen film samples (g); W_d is the weight of dry samples (g). The
 154 measurements were repeated three times for each type of film.

155 2.3.6. Study on surface hydrophobicity of the films

156 The surface hydrophilic/hydrophobic properties of the ternary films were evaluated using a PG-
 157 X goniometer (PG-X, Switzerland) by a sessile drop method. Droplets of 5 µL deionized water
 158 were placed on the airside (upper side during casting) of the film using a precision micro-
 159 syringe. Five measurements were conducted for each film.

160 2.3.7. Surface color and opacity measurements

161 The color of the ternary films was determined by a colorimeter (BYK Gardner, USA).
 162 Measurements are expressed as L^* -value (lightness), a^* -value (redness/greenness), and b^* -value
 163 (yellowness/blueness). A white standard color plate ($L = 94.61$, $a = -0.89$ and $b = 0.57$) was used
 164 to calibrate the instrument and as a background during the measurements. An average of three
 165 measurements recorded for each film and used to calculate the total color difference (ΔE)
 166 according to Eq. (4)

$$\Delta E = \sqrt{(\Delta E^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2} \quad (4)$$

167 The opacity of the films was also calculated using the Eq. 5:

$$(5)$$

$$Opacity\ value = \frac{Abs_{600}}{x}$$

168 Where Abs 600 is the value of absorbance at 600 nm and x is the film thickness (mm).

169 2.3.8. *Light transmission*

170 Light transmittance through the films (1 × 4 cm) was measured at the ultraviolet and visible
171 range (200-800 nm) using a UV-vis spectrophotometer (UV-2600, Shimadzu, Kyoto, Japan)
172 according to the method described by Fang, Tung, Britt, Yada, and Dalglish (2002).

173 2.3.9. *Fourier-transform infrared (FT-IR) spectroscopy*

174 FT-IR spectroscopy was conducted using a Perkin-Elmer Spectrum One spectrometer (Shelton,
175 CT, USA) to identify the chemical structure of the CH/PVA/FG ternary films and the possible
176 interactions between their components. Before analysis, the film samples were kept in a
177 desiccator containing silica gel for 1 week at room temperature to obtain maximally dehydrated
178 films. FT-IR spectra of the films were recorded at wavenumber range of 400-4000 cm⁻¹.

179 2.3.10. *X-ray diffraction (XRD)*

180 A Siemens D5000 X-ray diffractometer with Cu-K α radiation (λ = 1.78901 nm) accelerated at
181 voltage and current of 40 kV and 40 mA, respectively, was used to examine the crystallography
182 of the prepared films. The XRD pattern was collected over the 2θ scanning range of 5-80° at a
183 step size of 0.02°/min.

184 2.3.11. *Thermal characterization*

185 Differential scanning calorimetry (DSC) was performed on a DSC-200 F3 (NETZSCH,
186 Germany) under a nitrogen atmosphere at a flow rate of 100 mL/min. Samples (7.0 mg) were
187 sealed in aluminum pans and heated from 25 to 400 °C, with a heating rate of 10 °C/min.

188

189 2.3.12. *Scanning electron microscopy (SEM)*

190 Morphological observations of the surface and cross-section of the CH/PVA/FG ternary films
191 were performed by a scanning electron microscope (XL30 ESEM, Philips, Netherlands). For
192 cross-section, the films were immersed in liquid nitrogen and cryo-fractured manually. Then the
193 samples were fixed on aluminum stub using double-sided tape and were sputter-coated with a
194 thin layer of gold before imaging. SEM images were acquired with an accelerating voltage of
195 20 kV and the magnification of 1000 $\times$.

196 2.3.13. *Atomic force microscopy (AFM) imaging*

197 Atomic force microscope (CP-R, Veeco Instruments, USA) was utilized to evaluate the surface
198 morphology of the films with a 30 $\times$ 30 μ m scan size. These images were scanned in contact
199 mode under ambient conditions by triangular cantilever with a spring constant of 50 N/m. Two
200 statistical parameters, associated with sample's roughness, were calculated: average roughness
201 (R_a), and the root-mean-square roughness (R_q).

202 2.3.14. *Statistical analysis*

203 The statistical analysis was carried out using SPSS software (version 16.0 for Windows, SPSS
204 Inc., Chicago, IL, USA). The statistically significant differences among different variables were
205 performed using a one-way analysis of variance (ANOVA) followed by least significant
206 difference (LSD) test to establish if a significant difference exists ($p < 0.05$). Data were drawn by
207 Origin Pro 2018.

208

209

210 3. Results and discussions

211 3.1. Mechanical properties

212 The mechanical strength and flexibility are key parameters needed for food packages to keep
213 their integrity and tolerate external stress during their transport and exposition lifecycle. Fig. 2
214 displays the representative stress-strain (σ - ε) curves of ternary films, while the corresponding
215 tensile properties are listed in Table 1. From Fig. 2, a gradual/linear drawing process in the
216 stress-strain in CH/PVA and ternary films was clearly visible. The incorporation of 20% FG to
217 the films made them tougher as well as more elastic and led them to break at a higher
218 deformation degree; however, the 25CH/25PVA/50FG ternary film showed the lowest strength
219 and elongation values. This suggests the existence of specific intermolecular interactions
220 between CH, PVA and FG (Han, 2014), making the ternary film structure stronger and more
221 flexible. As the proportion of FG continued to increase, excess FG molecules were present in the
222 free form in the ternary films, resulting in a decrease in tensile values; this deduction has been
223 well examined by Zhang et al. (2019) for composite films based on rapeseed protein hydrolysate
224 and chitosan.

225 As presented in Table 1, the TS of the CH/PVA binary film was 36.74 ± 6.52 MPa. For ternary
226 films, as the FG content is increased, the TS represent an initial increase followed by a decrease
227 (Table 1); the maximum TS for the ternary films was 41.93 ± 3.24 MPa when the FG
228 concentration was 20%. As the TS is dependent on microstructure and intermolecular forces,
229 changing the ratios of FG may have resulted in reduction of TS; this may also be related to the
230 increased stress in the continuous phase arose from the higher amount of protein, resulted in the
231 lack of the stress transfer across the blend matrix interface, which reduced the strength of the

ternary film (Shahbazi, Rajabzadeh, & Ahmadi, 2017). However, the TS of these ternary films were higher than those of agar/alginate/collagen films (20.5-25.8 MPa) prepared by solvent casting method (Wang & Rhim, 2015), and comparable with typical packaging plastics, such as LDPE (low-density polyethylene) (15.2-78.6 MPa), and HDPE (high-density polyethylene) (17.9-33.1 MPa) (Castilho, Mitchell, & Freire, 2009).

Elongation-at-break (EAB), which is determined at the point where the film breaks under mechanical testing, gives information about the film's flexibility/stretchability (Bonilla et al., 2014). The EAB of control CH/PVA film was $94.12 \pm 14.27\%$ (Table 1), which is more than 2 times higher than the values reported by Wu, Ying, Liu, Zhang, and Huang (2018) for such films ($41.16 \pm 5.43\%$), and increased to a maximum value of $133.13 \pm 13.23\%$ when the FG content was 20%; however, the film flexibility was not significantly affected by increasing the levels of gelatin (Table 1). So, the optimum level of interaction between CH/PVA and FG was found in 40/40/20 ratio, which possessed the best mechanical properties (stronger and more flexible than the control polymer films as well as the other ratios).

3.2. Water vapor permeability (WVP)

Moisture transmission between the external and internal environment of a food product's package may result in reduced shelf-life; thus, WVP test is required to evaluate the ability of such biodegradable films in preventing penetration of water vapor through the package, since natural materials are mostly hydrophilic and composed of polar groups (Gontard et al., 1992). The WVP value of the control CH/PVA film was $0.686 \pm 0.008 \text{ g mm/kPa h m}^2$. As shown in Table 1, the WVP of FG incorporated (20-50%) ternary films significantly increased ($p < 0.05$), from 0.785 ± 0.053 to $0.818 \pm 0.037 \text{ g mm/kPa h m}^2$, indicating hydrophilic nature of gelatin and impact of hydrophilic-hydrophobic ratio of the film constituents on WVP (Abdelhedi et al.,

2018). It was also assumed that when FG was added, reduced intermolecular hydrogen bonds between CH and PVA molecules, resulted in more surface polar groups exposed to water vapor (Aguirre-Loredo, Rodríguez-Hernández, Morales-Sánchez, Gómez-Aldapa, & Velazquez, 2016). The WVP value obtained in the present study is several times lower than those reported for instance for agar/alginate/collagen ternary film, i.e., 5.44 g mm/kPa h m² (Wang & Rhim, 2015). Interestingly, when compared to synthetic polymer films, the values are approximately similar to the permeability value observed in cellophane films (0.248 g mm/kPa h m²) but higher than that observed in LDPE films (0.0072 g mm/kPa h m²).

3.3. Water solubility (WS)

Solubility is considered as an indicator of the resistance of the film samples to water, which is an important parameter for food packaging due to high water activity and the probability of contamination in the presence of water (Gontard et al., 1992). As can be seen in Table 1, the solubility of control CH/PVA films in distilled water was around 75%, which was higher than those presented in the literature for the composite films based on these polymers (57.3%) (Hajji et al., 2016). The discrepancy between studies can be due to the difference of polymer concentration and the used film-making procedures, which could affect the final properties of the resultant films (Cazón, Vázquez, & Velazquez, 2018). The addition of FG improved the water resistance of CH/PVA/FG ternary films, with pronounced changes produced from the 40CH/40PVA/20FG mass ratio (around 23%), indicating that this proportion might be an optimum composition. The interactions between molecules caused by electrostatic forces and hydrogen bonding may be the cause of solubility reduction; on the other hand, the addition of FG led to the formation of hydrogen bonds between protein and CH/PVA molecules, which reduced

the number of free hydroxyl groups in the ternary films and limited polymer molecules from binding to water molecules via hydroxyl groups (Liu, Wang, Lan, & Qin, 2019).

3.4. Swelling ratio (SR)

The knowledge of the swelling is also important for the design of packages and predictions of stability and quality changes that may occur during storage (Andrade, Lemus, & Perez, 2011). Since CH, PVA and FG are hydrophilic, water plays an important role (due to its ideal plasticizing effect). As summarized in Table 1, the control CH/PVA film displayed the lowest SR (230.9%) probably due to the formation of intra/inter-molecular interactions through hydrogen bonding between hydroxyl groups of CH and C=O groups of the remaining vinyl acetate units in the PVA backbone (Pereira Jr, de Arruda, & Stefani, 2015). With increasing levels of FG, a significant increase in SR ($p < 0.05$) was observed (the range being 445.24 ± 8.11 to $874.10 \pm 32.38\%$) (Table 1), which may be attributed to the great water uptake capacity of gelatin (due to presence of polar peptides) (Kavoosi, Dadfar, & Purfard, 2013). However, it is worth noting that all developed ternary films maintained their integrity up to the end of the swelling test.

3.5. Surface wettability

The surface wettability and hydrophilicity of the CH/PVA/FG ternary films were examined by measuring the contact angle (CA) of water droplet deposited onto the film's surface and the results are shown in Table 1. The CA value of the control CH/PVA film was 74.9° , higher than the value reported in the literature for CH/PVA film (62.7° at $\theta_{t=0}$) (Zhuang et al., 2018). CA values decreased with the increasing volume fraction of FG, which is mainly related to the hydrophilic nature of the protein. However, it is important to note that all developed films

possessed hydrophobic surfaces as they exhibited contact angles $\theta > 65^\circ$ (Hambleton et al., 2009); high CA values and hydrophobicity are crucial for several bio-related applications and especially for food packaging purposes.

3.6. Optical parameters

The color and opacity can directly affect food appearance and consumer's satisfaction and are thus two important parameters for packaging films (Zhang et al., 2018). The values of L^* , a^* , b^* , and ΔE^* , and opacity of the films are shown in Table 2. Visually, both control film and ternary films were clear and transparent; however, some differences in the CIELab coordinates and full-color variation between all films were observed (Table 2). The apparent color of the film samples determined by Hunter color values indicates that the ΔE of the neat CH/PVA film slightly decreased after formation of the ternary system by FG inclusion (Table 2), which is mainly due to the increase in Hunter L - and a -values and decrease in b -values. In terms of opacity, the obtained value for the CH/PVA binary film was 0.55 ± 0.05 AU/mm (Table 2). As summarized in Table 2, increasing the levels of FG resulted in higher opacity ($p < 0.05$), i.e. less transparency, in the resultant ternary films. The increase in opacity may have been the result of contraction of the film matrix in which the polymer inter-chain spacing was decreased, permitting less light to pass through the film (Yang, Paulson, & Nickerson, 2010).

3.7. Light transmittance of the ternary films

Since one of the common oxidation initiators in food systems is UV light (in the range of 200-280 nm), paying attention to the oxidation of lipids due to UV light is important (Guo, Ge, Li, Mu, & Li, 2014). The transmission of UV and visible light at a selected wavelength (200-800 nm) of the CH/PVA and the ternary films are shown in Fig. 3. The transmission of UV light was

very low at 200 nm for all films (0.08-0.11%), and at 280 nm in the ternary films the transmission decreased from 40.78 to 19.66% when FG content was increased from 20 to 50%; this may be attributed to the high content of aromatic amino acids such as tyrosine and tryptophan in the protein-based structure and, in a less extent, phenylalanine and disulfide bonds, that are able to absorb radiation (Aitken & Learmonth, 1996). These results were consistent with previous reports which showed that the FG-based films have excellent UV light barrier capacity (Hosseini, Rezaei, Zandi, & Farahmandghavi, 2015; Nilsuwan, Benjakul, & Prodpran, 2018), and so can prevent UV light-induced lipid oxidation when applied in food systems (Bonilla et al., 2014).

As depicted in Fig. 3, all CH/PVA/FG ternary films showed lower transmission of visible light in the range of 350-800 nm, compared to the control film, confirming that FG-incorporated films were slightly lower in transparency. This was consistent with the increase in opacity of films containing FG (Table 2). It can be concluded that FG with a high light transmission barrier ability most likely contributed to the limited light transmittance of the ternary films at both UV and visible ranges, and is more suitable for food packaging applications. Although the transmittance of the ternary films decreased with increasing FG content, the films still had good optical properties as shown in Fig. 3.

3.8. FT-IR spectra

The interactions between the molecules of the blends were analyzed by FT-IR measurements. The spectra of films from pure compounds and selected formulations are shown in Fig. 4. FT-IR spectrum of plain CH film exhibited characteristic bands at 3367, 2878, 1654, 1565 and 1379 cm^{-1} , assigned to the O-H and N-H stretching, C-H stretching, C=O stretching of amide group (amide I), N-H bending (amide II) and CH_3 symmetrical deformation, respectively (Kaur &

Jindal, 2019; Zhang et al., 2018); the absorption band at 1153 cm^{-1} was ascribed to the saccharide structure of polysaccharide. In the PVA film spectrum, the strong and broad absorption peak at about 3339 cm^{-1} was ascribed to the stretching vibration of O-H groups (Yu, Li, Chu, & Zhang, 2018). The two sharp peaks at 2941 and 1735 cm^{-1} were assigned to the asymmetric stretching mode of C-H (Ma, Du, Yang, & Wang, 2017) and stretching vibrations of C=O groups of the remaining vinyl acetate units in the PVA backbone (Wu et al., 2018), respectively. Meanwhile, the absorption bands presented at 1431 and 1249 cm^{-1} can be assigned to the O-H bending and C-O-C band stretching vibration (Cazón et al., 2018), respectively. The peaks at 1098 and 851 cm^{-1} also corresponded to the C-O stretching vibrations and expansion of C-O, respectively (Ma, Du, Yang, & Wang, 2016). In contrast, the characteristic peaks of the pure FG film included a peak caused by N-H stretching (amide A) vibration at wavenumber 3300 cm^{-1} , a peak caused by C=O stretching (amide I) vibration at 1651 cm^{-1} , and a peak caused by N-H bending (amide II) vibration at 1544 cm^{-1} .

The infrared spectra of CH/PVA blend films exhibited the characteristic peaks of both polymers; however, some of the peaks were shifted to lower and higher frequencies (Fig. 4). For example, the shift of amide III peak (1249 cm^{-1}) in PVA to higher wavenumber (1254 cm^{-1}) in the composite films, together with the downshift of the bending vibration of O-H in PVA (1431 cm^{-1}) and the asymmetric stretching of the C-O-C bridge (1153 cm^{-1}), suggested intermolecular interactions between CH and PVA molecules (Ma et al., 2008). According to Zhang et al. (2019), the lack of new peaks in the CH/PVA composite film compared with that of the pure films, indicated that CH was compatible with PVA ().

When FG was added to the CH/PVA matrices, the absorption peak of O-H shifted to a lower wavenumber (Fig. 4), indicating an increase in hydrogen bonds which enhanced the tensile

properties of biodegradable films at the optimum ratio (i.e. 40CH/40PVA/20FG) (Yu et al., 2018). Meanwhile, the band at around 1735 cm^{-1} shifted to a lower wavenumber and/or disappeared in the spectrum of CH/PVA/FG film (Fig. 4), instead, the intensity of C=O stretching band at 1654 cm^{-1} increased with increasing protein fraction in the ternary systems. Furthermore, after incorporation of FG, the amplitude of peaks at wavenumbers of 1566, 1420, 1376, and 1254 cm^{-1} decreased; this was presumably due to the formation of various kinds of intra/inter-molecular hydrogen bonds among N-H and O-H groups (Wang et al., 2018). Also, the absorption peak at about 1088 cm^{-1} corresponding to the C-O group (Pereira Jr et al., 2015) shifted to 1045 cm^{-1} . The above-observed phenomenon of FT-IR implied that interactions occurred between functional groups (O-H and N-H) of the three polymers in the blends, which enhanced the compatibility between the polymeric phases.

3.9. X-Ray Diffraction

XRD analysis was carried out to monitor a possible change of crystallinity of obtained ternary films and assess the compatibility of different components. As shown in Fig. 5, the XRD pattern of pure CH displays two main diffraction peaks at $2\theta = 10.07^\circ$ (corresponding to crystal I) and 23.71° , (corresponding to crystal II) typical of its semi-crystalline nature (Kaur, Jindal, & Jindal, 2018; Liu, Cai, Sheng, Ma, & Xu, 2019), while PVA showed a sharp crystallographic reflection at $2\theta = 22.82^\circ$ and a weak peak around 46.8° (Yun, Kim, Shim, & Yoon, 2018). Neat FG film exhibited an XRD pattern characteristic of a partially crystalline material (Fig. 5), with two defined diffraction peaks, the first in the region of $2\theta = 10.31^\circ$, corresponding to the crystalline triple helix structure of gelatin, and a second broad peak at $2\theta = 23.58^\circ$, characteristic of an amorphous phase (Pérez-Córdoba et al., 2018). Fig. 5 showed the crystal structure of the film was slightly changed when PVA was blended with CH; comparing with pure CH film, the

crystalline peak of crystal II at $2\theta = 23.71^\circ$ became more intense and/or sharper. This phenomenon illustrated that the addition of PVA had ability to enhance the crystal growth of CH. However, there was no newly sharp peak observed over the range of 2θ degree in ternary films with FG, suggesting that there was good compatibility and interaction among different components in the films (Pérez-Córdoba et al., 2018).

3.10. Thermal properties of the ternary films

The DSC curves of the pure ingredients and the selected ternary films along with the results of thermal parameters determined from the DSC thermograms are depicted in Fig. 6. Two endothermic peaks were detected for all films; the first sharp endothermic peak over the temperature range of 126.9-197.8 °C may be assigned to the overlapping of different phenomena, such as volatilization of adsorbed water, residual acetic acid, degradation of the plasticizer, helix-coil transition of gelatin, as well as melting temperature (T_m) of polymers (Nilsuwan et al., 2018; Zhang et al., 2018), while the second broad peak in the range of 266.3-318 °C represented the thermal decomposition (T_d) due to dehydroxylation of the PVA, pyrolytic decomposition of the CH backbone, and the thermal decomposition of peptide bonds in the main chain of gelatin (Martucci & Ruseckaite, 2015; Zohuriaan & Shokrolahi, 2004). Regarding the films prepared from pure ingredients, the melting peaks of CH, PVA and FG at 175.3, 197.8, and 126.9 °C were in the range of documented values (Hosseini, Nahvi, & Zandi, 2019; Liu et al., 2019; Nilsuwan et al., 2018), respectively. Compared to the melting point of pure CH, endothermic peaks of the CH/PVA blend films were shifted towards higher temperatures (Fig. 6), which pointed out the good miscibility of both macromolecules (Bonilla et al., 2014). With regard to FG-doped ternary films, reduced T_m and T_d values suggested increasing the mobility of the macromolecules in the amorphous regions, thus slightly decreasing thermal stability.

3.11. Films morphology

In an attempt to study the homogeneity and microstructural changes in the developed films, SEM was conducted to visualize the surface and cross-section topography of different ternary films prepared from CH, PVA, and FG, at different ratios. Control and films with FG up to 30% (i.e. 40/40/20 and 35/35/30 ratios) display relatively smooth and homogeneous surfaces, without pores and/or cracks, indicating the compatibility of the three polymers; however, the presence of small micro-particles could be observed at the surface of the films (Fig. 7). As could be seen from Fig. 7, a different surface arrangement was observed when 40 and 50% FG was added to the film matrices (i.e. 30/30/40 and 25/25/50 ratios). Meanwhile, the cross-sectional images of both the control and the ternary films showed a continuous and compact morphology with no irregularities (like air bubbles or pores), and without any evidence of phase separation, as expected for a homogeneous material (Fig. 7). The obtained structure can be due to the intermolecular polymer associations through the hydrogen bond formation or may be due to the good compatibility between CH, PVA, and FG, which improved the miscibility of the ternary system (Bonilla et al., 2014). This may be explained by the improved mechanical and barrier properties of the ternary films at an optimum proportion (i.e. 40CH/40PVA/20FG ratio).

3.12. Surface morphology analysis

AFM was further conducted to characterize the surface morphology of the obtained ternary films; furthermore, AFM allows a histogram to be plotted of the relative height of every pixel recorded during the scan (Mohajer, Rezaei, & Hosseini, 2017). Typical 3D surface topographic AFM images together with the corresponding height profiles are presented in Fig. 8. The surface morphologies of the CH/PVA/FG ternary films were dependent on the FG concentration as it

may be seen in the AFM images presented in Fig. 8a-c. The images clearly demonstrate a re-organization of the surface of the ternary films, which supported the results of SEM images. As can be seen from Fig. 8a, the control CH/PVA film showed the relatively smoother surface and homogeneous morphology as indicated by lower R_a , R_q , and peak height values (2.01, 3.11 nm and 64.5 nm, respectively), while for the ternary films, the surface was rougher (i.e., more wrinkles), presenting a more complex superficial topography (Fig. 8b & c). The aggregation of polymer chains would influence the surface morphology of the ternary films. It has been proposed that this trend is potentially due to the establishment of some interactions between polymer chains by electrostatic forces, hydrogen bonding, etc. (Guerrero, Garrido, Leceta, & de la Caba, 2013). Nonetheless, the height profiles showed that the ternary film with the replacement of 50% CH/PVA by FG (i.e. ratio 25/25/50) had a maximum vertical distance of 196 nm (Fig. 8c), which may be associated to the greater development of polymer aggregation during the drying step, and consequently producing irregularities on the film's surface.

4. Conclusions

In this study, the ternary CH/PVA/FG films were prepared by the casting method and their features were assessed. Structural properties assessment by FT-IR, XRD, DSC, SEM, and AFM showed interactions between CH, PVA, and FG, leading to the formation of a new composite material with improved physicochemical characteristics. According to the FS, TS, EAB, and opacity values, the optimum ratio was 40CH/40PVA/20FG. Therefore, this formulation could be used to produce ternary films for food packaging purposes.

Acknowledgments

The study has been carried out with the financial support from Research Council of Tarbiat Modares University.

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605 **Figure captions**

606 **Fig. 1.** Schematic illustration of the preparation process of the CH/PVA/FG ternary films.

607 **Fig. 2.** Typical stress-Hencky strain curves of the CH/PVA/FG ternary films at selected
608 proportions.

609 **Fig. 3.** Light-transmittance curves of the CH/PVA/FG ternary films at different proportions.

610 **Fig. 4.** FT-IR spectra of the CH/PVA/FG ternary films at selected proportions.

611 **Fig. 5.** DSC thermograms of the CH/PVA/FG ternary films at selected proportions.

612 **Fig. 6.** SEM images of the surface and cross-section of the CH/PVA/FG ternary films at different
613 proportions.

614 **Fig. 7.** 3D AFM images together with the corresponding height profiles of the CH/PVA/FG
615 ternary films at selected proportions.

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617 **Table 1**

618 Tensile strength (TS), elongation-at-break (EAB), water vapor permeability (WVP), film solubility (FS), and swelling

CH/PVA:FG ratio	TS (MPa)	EAB (%)	WVP (g mm/kPa h m ²)	FS (%)	SR (%)
50CH/50PVA:0FG	36.74 ± 6.52 ^a	94.12 ± 14.27 ^a	0.686 ± 0.008 ^a	75.26 ± 6.37 ^a	230.90 ± 15.35 ^a
40CH/40PVA:20FG	41.93 ± 3.24 ^a	133.13 ± 13.23 ^b	0.785 ± 0.053 ^b	58.03 ± 6.39 ^b	445.24 ± 8.11 ^b
35CH/35PVA:30FG	27.76 ± 0.68 ^b	97.78 ± 11.90 ^a	0.837 ± 0.047 ^b	64.02 ± 2.75 ^b	493.03 ± 18.64 ^c
30CH/30PVA:40FG	27.48 ± 4.91 ^{bc}	94.83 ± 6.82 ^a	0.829 ± 0.024 ^b	62.39 ± 0.22 ^b	728.90 ± 22.19 ^d
25CH/25PVA:50FG	25.90 ± 1.21 ^{bc}	89.36 ± 4.69 ^a	0.818 ± 0.037 ^b	61.31 ± 0.73 ^b	874.10 ± 32.38 ^e

619 ratio (SR) of the CH/PVA/FG ternary films at different proportions.

620 Values are expressed as the mean ± standard deviation. Superscripts bearing different lower case letters in the same column
621 indicate significant differences ($p < 0.05$).

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Table 2

Contact angle at initial time ($\theta_{t=0}$) and after 10 s ($\theta_{t=10}$) along with photographs of the interaction between the drops

Film	$\theta_{t=0}$ (°)	Image	$\theta_{t=10}$ (°)	Image
(50CH/50PVA:0FG)	74.95 ± 2.61^a		83.35 ± 2.33^a
(40CH/40PVA:20FG)	73.85 ± 2.76^a		79.65 ± 0.49^a
(35CH/35PVA:30FG)	73.25 ± 2.33^a		78.7 ± 1.83^a
(30CH/30PVA:40FG)	72.95 ± 3.32^a		77.1 ± 3.11^a
(25CH/25PVA:50FG)	72.65 ± 0.21^a		76.8 ± 1.90^a

of deionized water and the surface of the CH/PVA/FG ternary films at different proportions.

Values are expressed as the mean $\pm$ standard deviation. Superscripts bearing different lower case letters in the same column indicate significant differences ($p < 0.05$).

Table 3

Color parameters (CIELab) and total color difference (ΔE), and opacity values of the CH/PVA/FG ternary films at different proportions.

Film	Color parameters				Opacity (UA/mm)	Values are expressed as the mean $\pm$ standard deviation.
	L^*	a^*	b^*	ΔE		
50CH/50PVA:0FG	27.46 $\pm$ 0.05 ^a	3.68 $\pm$ 0.04 ^a	8.56 $\pm$ 0.42 ^a	67.59 $\pm$ 0.27 ^a	0.55 $\pm$ 0.05 ^a	
40CH/40PVA:20FG	28.11 $\pm$ 0.07 ^b	3.64 $\pm$ 0.05 ^a	7.71 $\pm$ 0.10 ^b	67.04 $\pm$ 0.07 ^b	1.37 $\pm$ 0.05 ^b	
35CH/35PVA:30FG	28.39 $\pm$ 0.13 ^c	3.67 $\pm$ 0.22 ^a	7.68 $\pm$ 0.15 ^b	66.56 $\pm$ 0.35 ^c	1.82 $\pm$ 0.06 ^b	
30CH/30PVA:40FG	28.23 $\pm$ 0.03 ^{bc}	3.75 $\pm$ 0.07 ^a	7.98 $\pm$ 0.39 ^b	67.17 $\pm$ 0.32 ^{ab}	3.25 $\pm$ 0.06 ^d	
25CH/25PVA:50FG	27.97 $\pm$ 0.01 ^b	3.77 $\pm$ 0.08 ^a	7.82 $\pm$ 0.20 ^b	67.28 $\pm$ 0.14 ^{ab}	4.03 $\pm$ 0.06 ^e	

Superscripts bearing different lower case letters in the same column indicate significant differences ($p < 0.05$).

Fig. 1.

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Fig. 5.

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<p>50CH/50PVA:0FG</p>

<p>40CH/40PVA:20FG</p>

<p>35CH/35PVA:30FG</p>

<p>30CH/30PVA:40FG</p>

<p>25CH/25PVA:50FG</p>

Fig. 6.

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857 **Fig. 7.**

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