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Research article

Thermal curing to improve properties of genipin-crosslinking chitosan film

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Abstract

Importance of the work: Chitosan film as a natural biodegradable packaging material has limited food applications due to its high moisture permeability and poor mechanical strength. Crosslinking with genipin, a natural crosslinker, and thermal curing were applied to eliminate these drawbacks.

Objective: To study the effect of the genipin concentration and thermal curing on the chemical structure and properties of chitosan film.

Materials & Methods: Chitosan (CS, 1.5 g) solution were prepared crosslinked with genipin at 0.5%, 1.0% or 1.5 (all weight per weight, w/w of chitosan) % and cured at 25 °C, 80 °C or 105 °C. Film properties were investigated: water vapor permeability (WVP), tensile strength (TS), elongation at break (EAB), Young's modulus (YM), thermal stability, crystallinity and contact angle.

Results: Increasing the genipin concentration significantly increased the degree of crosslinking, TS and YM of the films, with the best film obtained at 1.5% w/w genipin (CS1.5G). The CS1.5G film with curing at 105 °C (CS1.5G-105) had the highest ($p < 0.05$) TS (36.45 MPa), YM (315.99 N/m^2) and thermal stability due to a high conjugation of C double bonding between the genipin molecules in the chitosan chains. However, CS1.5G-105 decreased the crystallinity, EAB and WVP, while the contact angle value increased.

Main finding: Improving properties, such as the mechanical strength and moisture barrier of the genipin-crosslinked film, could be achieved by thermal curing, thus increasing the potential of the film for use as food packaging in the food industry.

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Introduction

Chitosan, a natural polysaccharide formed between *β*-(1-4)-linked 2 acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose, generally deacetylated from the chitin of crustaceans, has been used for numerous applications in the food industry, particularly as a packaging material due to its available film-forming, biocompatible and biodegradable properties (Varun et al., 2017; Venkatesan et al., 2017). Chitosan with its functional properties of being bacteriostatic and fungistatic, has potential to be applied as active packaging (Dutta et al., 2009; Martins et al., 2012) to extend the shelf life of food. Chitosan film has a good oxygen barrier property (Azeredo et al., 2011). However, its poor mechanical properties limit its practical applications for food packaging. Modifying the chitosan matrix through a crosslinking structure is applied to overcome these drawbacks by enhancing the mechanical strength through forming chemical bridges at amine groups of the chitosan (Khouri et al., 2019). The most common synthetic chemicals used as crosslinking reagents are aldehyde substances, such as glyoxal (Yang et al., 2005), glutaraldehyde (Li et al., 2013) and formaldehyde (Xue et al., 2011). However, these substances are reported to have a certain degree of toxicity due to the presence of both unreacted molecules of such crosslinkers and by-products formed during the reactions (Dimida et al., 2015). Therefore, an alternative natural crosslinker, such as genipin, has attracted substantial interest.

Genipin is a natural crosslinking agent isolated from the fruit of *Gardenia jasminoides* Ellis which can be used to replace the synthetic-chemical crosslinker because it is safe and nontoxic and therefore it is primarily used as scaffolds and hydrogel in tissue engineering and pharmaceutical applications (Jin et al., 2004; Xu et al., 2015; Dimida et al., 2017). The crosslinking reaction between genipin and the amino groups of chitosan can be formed with a covalent bond, resulting in improved mechanical properties, as well as thermal stability of the resulting chitosan film (Butler et al., 2003; Nunes et al., 2013; Wu et al., 2018; Liu et al., 2019). However, the reaction is sometimes incomplete and not rapid enough for some applications. To finalize the crosslinking process, curing processes have been studied, using ultraviolet light (Yun et al., 2017), electromagnetic waves (Biswas et al., 2017), pressure (Gan et al., 2020) or heat (Dimida et al., 2015).

Many investigations have focused on the use of heat curing method because it is easy, safe and inexpensive and has been reported to increase the kinetic rate of polymerization and to stabilize the biopolymer network (Dimida et al., 2015; Rubentheren et al., 2016). In addition, some authors reported that heat curing improved the mechanical, thermal stability and moisture barrier properties of the polymer (Rivero et al., 2011; Falamarzpour et al., 2017). Although genipin has been reported as a crosslinking agent in chitosan films, few studies have been conducted on the chemical-crosslinking structure and the properties of genipin-crosslinking chitosan film under thermal treatment. Thus, this study evaluated the effect of the genipin concentration and thermal curing on the morphology, moisture barrier, mechanical properties, crystallization and thermal stability of the film.

Materials and Methods

Materials

Chitosan (MW: 50-190 KDa) was purchased from Sigma-Aldrich, USA. Genipin (purity = 99.1%) was ordered from Tokyo Chemical Industry Co., Ltd, Japan.

Film preparation

The genipin was evaluated as a natural crosslinking agent. In this study the optimal genipin concentration was determined by adding genipin at different concentrations into chitosan film (CS) solution and observing the properties of the resulting films. An amount of chitosan (1.5 g) as melted in 100 mL aqueous solution containing lactic acid at 2% (weight per weight, w/w) and then homogenized using a magnetic stirrer (Corning PC-420D; Korea) at 500 revolutions per minute and 25 °C until the solution was clear. Genipin concentrations at 0% (CS), 0.5% (CS0.5G), 1.0% (CS1G) or 1.5 (CS1.5G)%, (all w/w of chitosan) were mixed in chitosan solution for 45 min. The mixture solution was added with 15% (w/w of chitosan) of glycerol, stirred at 50 °C for 15 min and the gas was removed using an ultrasonicator (Sonicator bath 500 series; Powersonic Hwashin Co. Ltd.; Korea) for 30 min. A sample volume of film solution (100 mL) was poured onto a polytetrafluoroethylene tray (125 mm × 125 mm × 20 mm) and then dried in a hot air oven (400D-003, TESTONE Co., Ltd.; Korea) at 35 °C for 48 h. The films were maintained under controlled conditions of 50% relative humidity (RH) at 25 °C for 24 h. Characterization of film samples was carried out of the crosslinking degree and functional properties: vapor permeability (WVP), tensile strength (TS), elongation at break (EAB) and Young's modulus (YM).

Thermal curing

The influence of thermal curing on the chemical-crosslinking structure and properties of CS and the crosslinked film (obtained from the optimal crosslinking condition: CS1.5G) were investigated by curing the films (CS and CS1.5G) at 25 °C, 80 °C or 105 °C for 30 min, according to the method of Falamarzpour et al. (2017) with slight modifications. All films were stored under controlled conditions at 25 °C, 50% RH for 24 h before measurement.

Measurement of film properties

Chitosan and the chitosan film crosslinked with genipin with and without thermal curing were characterized as follows.

Thickness

Each sample (50 mm × 50 mm) was measured for thickness at five random positions using a digital micrometer (M-547 Thickness Gage Series; Mitutoyo; Japan). Ten films were measured for each treatment, with the mean values calculated.

Crosslinking degree

The crosslinking degree was carried out following the 2,4,6-trinitrobenzene sulfonic acid (TNBS) assay method (Kanoujia et al., 2018). The mixture solution between 0.5% (weight per volume, w/v) TNBS and sodium hydrogen carbonate (4% w/v) solution was prepared at a 1:1 ratio; then, 1 mL of the mixed solution was added in a sample (6 mg) tube. The sample was cured at 40 °C for 2 h. To stop the reaction, 6 M of hydrochloric acid (3 mL) was added in solution and continuously cured at 60 °C for 90 min. The absorbance was measured at 345 nm using a spectrophotometer (Optizen 2120 UV; Mecasys Co. Ltd.; Korea). The percentage of crosslinking was calculated using Equation 1:

$$\%\ \text{Crosslinking} = \left(\frac{\chi NH2 - \chi NH2cross}{\chi NH2}\right) \times 100 \tag{1}$$

where $\chi NH2$ is he absorbance value at 345 nm of free amines in CS and $\chi NH2cross$ is the absorbance value at 345 nm for the crosslinked film (CS0.5G, CS1G or CS1.5G).

Fourier-transform infrared spectroscopy analysis

Fourier transform infrared (FTIR) spectroscopy was performed to note the chemical-crosslinking structure of chitosan and genipin. The FTIR spectra of films were recorded from 4000 cm^{-1} to 400 cm^{-1} with 4 cm^{-1} resolution and an accumulation testing at 32 scans using an FTIR spectrometer (Spectrum 65; Co., Ltd.; Korea), according to Dimida et al. (2017).

Moisture permeability

The water vapor permeability (WVP) was determined on the basis of a modified ASTM method E96-80 (American Society for Testing and Materials, 1992) as described by Siripatrawan and Vitchayakitti (2016). The WVP of each sample was investigated for four replications. An aluminum cup was determined as 0% RH using silica gel (20 g) and then covering with film at a radius of 30.06 mm. All samples were stored at 25 °C in desiccator (controlled at 75% RH with sodium chloride solution) and weighed intermittently to a steady state. The WVP (measure in grams millimeters per hour per aquare centimeter per pascal) was calculated according to Equation 2:

$$\text{WVP} = \frac{\Delta m}{\Delta t \text{A}} \times \frac{x}{\Delta \rho} \tag{2}$$

where $\frac{\Delta m}{\Delta t}$ is the slope from moisture weight gain per time unit (measured un grams per hour), A is the transferred area of film (in square millimeters), x is the thickness of film (in millimeters), and Δρ is the difference in water vapor pressure (in pascals) between the inner and outer surface of the film.

Contact angle measurement

The wettability on the surface sample was measured using an optical tensiometer (SDS-TEZD10014; FEMTOFAB Co., Ltd.; Korea). Each sample (20 mm × 40 mm) was placed on a glass plate and fixed with tape adhesive. Then 2 µL of water were dropped on the film surface. The angle (°) was measured to within 5 s to calculate the mean values of the test on both side of water droplet (Wu et al., 2018).

Mechanical properties

TS, EAB and YM were measured using a universal testing machine (MC Tester version 12.5.0; Quality & Measurement Systems; USA) according to the ASTM method D882-88 (American Society for Testing and Materials, 1992). Each sample (20 mm × 90 mm) was fixed in a specific grip. An initial separation distance was determined at 50 mm and the test speed was 50 mm/min. Fifteen films were investigated for each treatment.

Surface morphology

Film morphology was assessed using scanning electron microscopy (SEM; JSM-IT500HR; JEOL Ltd.; Japan) with an accelerating voltage at 5 kV. Each sample was coated with 1 nm of gold to improve conductivity (Dimida et al., 2017).

X-ray diffraction

The crystalline characteristics of the films were investigated using an X-ray diffractometer (D8 Discover; Bruker Co., Ltd.; Germany) according to the method of Rivero et al. (2011). Cu radiation, operated at 25 °C, was generated at 40 kV. The relative intensity was recorded for a scanning range of (2θ) 3–60º, with a step size $2\theta = 0.02°$.

Thermal stability

The thermal stability of the films was measured using a thermogravimetric analyzer-TGA (Pyris series-TGA4000, PerkinElmer Co., Ltd., Korea). Sample (10–11mg) was heated from 30 °C up to 800 °C at the rate of 20 °C min^{-1} under nitrogen atmosphere. The changes in sample weight with increasing temperature were recorded on the excel graph (Klein et al., 2016).

Statistical analysis

Statistical analyses were carried out using the IBM SPSS Statistics for Windows (Version 20.0; IBM Corp.; USA). To assess the effects of genipin concentrations on the film properties, data on thickness, crosslinking degree, TS, EAB and YM of control (CS) and crosslinked films were analyzed using one-way analysis of variance. Then, all data were subjected to two-way analysis of variance to test the effects of genipin-crosslinking, curing temperatures and their interaction. Subsequently, differences between treatments were analyzed using Duncan's multiple range test. Mean and standard deviations were analyzed at a significance level of $p < 0.05$.

Results and Discussion

Optimal genipin-crosslinking film

Film thickness is shown in Table 1. The addition of genipin concentrations did not affect the film thickness. The higher the genipin concentration, the darker the film color. CS1.5G

Table 1 Thickness, crosslinking degree, tensile strength (TS), elongation at break (EAB) and Youn's modulus (YM) of film crosslinked at genipin concentrations

Sample	Thickness (mm)	Crosslinking degree (%)	TS (MPa)	EAB (%)	YM (N/m²)
CS	0.172 ± 0.027^a	ND	7.610 ± 0.939^c	122.664 ± 11.017^a	8.810 ± 0.612^c
CS0.5G	0.167 ± 0.035^a	26.744^c	10.666 ± 1.307^b	106.222 ± 2.011^b	11.331 ± 2.422^c
CS1G	0.167 ± 0.039^a	55.814^b	12.087 ± 1.534^b	50.038 ± 8.625^c	77.196 ± 4.820^b
CS1.5G	0.166 ± 0.029^a	74.419^a	14.261 ± 1.372^a	44.246 ± 7.984^c	105.651 ± 4.185^a

CS = pure chitosan film; CS0.5G = chitosan crosslinked with 0.5% genipin; CS1G = chitosan crosslinked with 1% genipin; CS1.5G = chitosan crosslinked with 1.5% genipin

Mean (± SD) values within a column superscripted with different lowercase letters are significantly ($p < 0.05$) different; ND = not detected in studied samples had the darkest-blue color compared to the other film samples, probably due to the crosslinking reaction between genipin and chitosan being related with oxygen radical-induced polymerization, as similarly reported by Dimida et al. (2015) and Lee et al. (2003).

The crosslinking degree percentages of CS0.5G, CS1G and CS1.5G film were 26.74%, 55.81% and 74.42%, respectively, as shown in Table 1. The percentage degree of crosslinking increased as the crosslinker concentration increased, probably because of the reduction of the free amines within chitosan. This suggested that genipin as a crosslinking agent could form intermolecular crosslinking with chitosan (Kanoujia et al., 2018).

TS, EAB and YM are three important parameters to evaluate the strength and flexibility of biodegradable film (Jakubowska et al., 2020). In the current study, the values for TS, EAB and YM of non-crosslinked and crosslinked chitosan films are shown in Table 1. Increasing the genipin concentration significantly increased TS and YM, while EAB slightly decreased. The values for TS and YM of CS0.5G film increased by 28% and 22%, respectively, and increased by 37% and 88%, respectively for CS1G film, compared to those of the CS film. Moreover, CS1.5G had the highest values for TS and YM with increases of 47% and 91%, respectively, compared to the CS film. However, the EAB of films significantly decreased when the genipin was added, which was probably related to the crosslinking between chitosan and genipin by covalent bonding (C-N), as reported by Inthamat et al. (2021a), resulting in the films being more rigid.

The current results indicated that chitosan crosslinked with 1.5% genipin provided optimal film properties (TS and YM). Therefore CS1.5G was used further to study the effect of heat curing.

Effect of thermal curing on chitosan and crosslinked chitosan film

The CS and CS1.5G films were cured at 25 °C (CS-25 or CS1.5G-25), 80 °C (CS-80 or CS1.5G-80) or 105 °C (CS-105 or CS1.5G-105) and then were then analyzed for chemical structure, WVP, contact angle, TS, EAB, YM, crystallinity and thermal stability. Analysis of variance showed that thermal curing was the main effect causing a decrease in WVP and an increase in TS, EAB and YM for both the CS and CS1.5G films. There were significant interactions between thermal curing and genipin-crosslinking for TS, EAB and YM values of the films.

Fourier-transform infrared spectroscopy of thermal curing films

Fig. 1A displays the FTIR spectra of film cured at 25 °C, 80 °C and 105 °C. The signals observed at 1719 cm^{-1} and 1568 cm^{-1} were assigned to amide I (C=O stretching) and amide II (N–H stretching), respectively. Generally, the crosslinking between the amino groups at amide I and amide II of chitosan and the carbon atom at the C–3 position on the olefinic ring of genipin was formed as shown in the CS1.5G-25 film. The characteristic signals of CS1.5G-25 at 1723 cm^{-1} and 1571 cm^{-1} were shifted to 1725 cm^{-1} and 1574 cm^{-1} for CS1.5G-80. Similarly, these peaks were moved to 1728 cm^{-1} and 1577 cm^{-1} for CS1.5G-105. A peak at 1410 cm^{-1} of CS1.5G-80 and CS1.5G-105 was detected when those films had higher density due to heat curing, probably attributed to the C–C binding between the genipin molecules already linked to the amino groups of the chitosan chain (Inthamat et al., 2021b).

Water vapor permeability of thermal curing films

The CS-25 film had an WVP value of $2.79 \pm 0.19 \times 10^{-4}$ g mm/h/mm^2/Pa when cured at 80 °C and 105 °C; however, the WVP values of CS-80 and CS-105 were significantly reduced to $2.65 \pm 0.09\times10^{-4}$ g mm/h/mm^2/Pa and $1.95 \pm 0.13\times10^{-4}$ g mm/h/mm^2/Pa, respectively. Films crosslinked with genipin had lower WVP values than non-crosslinked films. For example, the WVP of CS-25 ($2.79 \pm 0.19\times10^{-4}$ g mm/h/mm^2/Pa decreased to $1.77 \pm 0.11\times10^{-4}$ g mm/h/mm^2/Pa after crosslinking with genipin (CS1.5G-25). The WVP of CS1.5G-80 significantly decreased from $1.77 \pm 0.11\times10^{-4}$ g mm/h/mm^2/Pa (CS1.5G-25) to $1.37 \pm 0.08\times10^{-4}$ g mm/h/mm^2/Pa when cured at 80°C. A similar trend was observed for the CS1.5G-105 film with curing at 105 °C, producing the lowest WVP value of $0.81 \pm 0.01\times10^{-4}$ g mm/h/mm^2/Pa compared with that of CS1.5G-25. These results agreed well with those obtained by Inthamat et al. (2021b) and Rivero et al. (2011) who reported that the molecular alterations in film structure due to curing at high temperatures, probably because the carboxylic acid could react with the amine group to form an amide resulting in water being eliminated (de Castro et al., 2013).

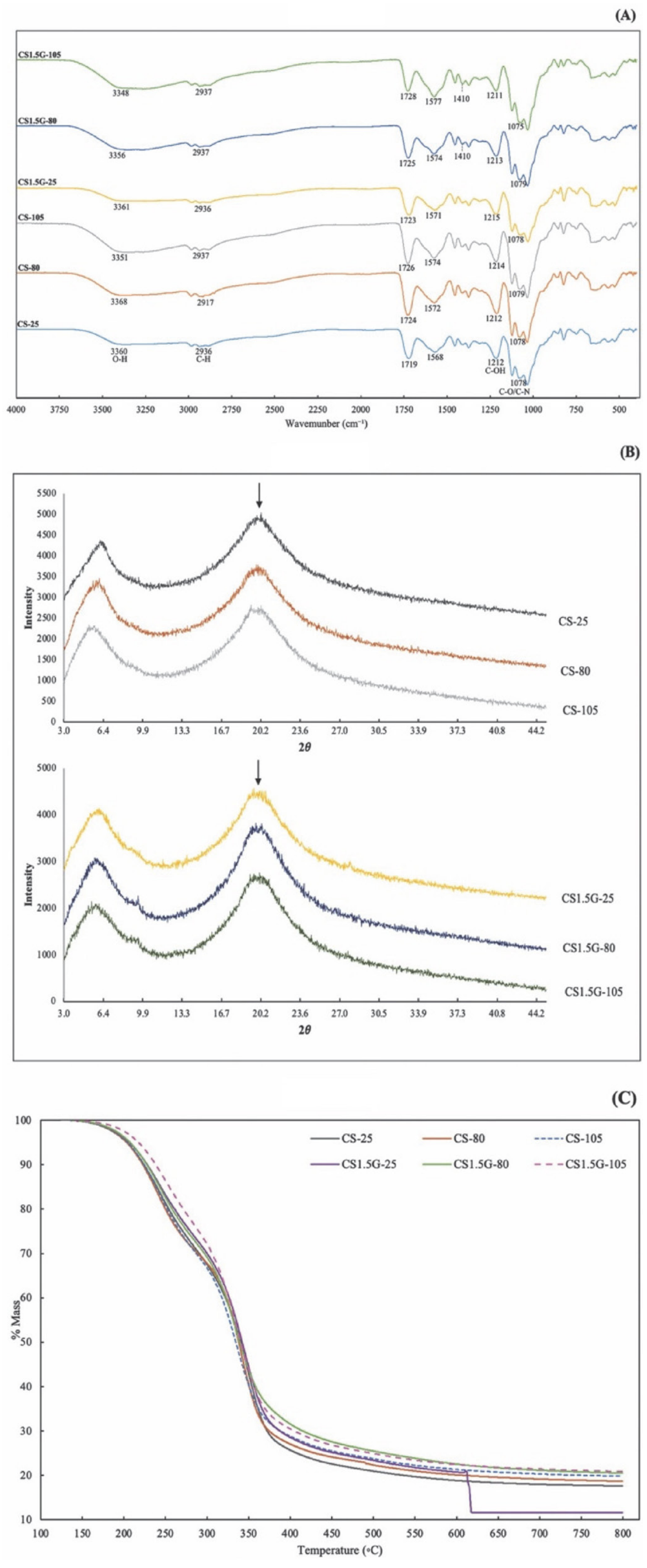

Fig. 1 Chitosan (CS) and CS with 1.5% w/w genipin (CS1.5G) films with curing temperatures at 25 °C, 80 °C or 105 °C: (A) Fourier-transform infrared spectra; (B) X-ray diffractometry; (C) thermogravimetric analyzer curves

Contact angle of heat curing films

A contact angle image of cured films is shown in Fig. 2; the contact angles increased gradually with increasing curing temperature. The CS-25 film had a value of 55.8° that the contact angles of crosslinked-chitosan film with increasing heat curing, with a value of 43.1° for CS1.5G-25, increasing to 54.9° for CS1.5G-80 and to 60.1° for CS1.5G-105, respectively. The cured films had the highest contact angle values, indicating that thermal curing played an important role in decreasing the hydrophilic nature of the film surface. Similar effect had been observed in the works of Rivero et al. (2013) and Czibulya et al. (2021).

Mechanical properties of thermal curing films

The values for TS, EAB and YM of CS and CS-1.5G film with curing temperature at 25 °C, 80 °C and 105 °C are shown in Table 2. The results indicated that curing the films

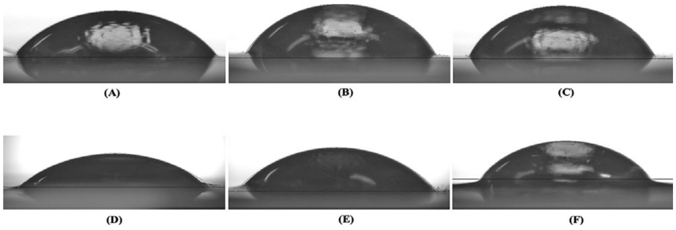

Fig. 2 Contact angles of chitosan (CS) and CS with 1.5% w/w genipin (CS1.5G) films with curing temperature at 25 °C, 80 °C and 105 °C: (A) CS-25; (B) CS-80; (C) CS-105; and for pure chitosan with curing at 25 °C, 80 °C and 105 °C: (D) CS1.5G-25; (E) CS1.5G-80; (F) CS1.5G-105, where chitosan is crosslinked with 1.5% genipin and cured at 25 °C, 80 °C and 105 °C, respectively.

Table 2 Tensile strength (TS), elongation at break (EAB) and Young's modulus (YM) of CS and CS1.5G film with curing temperatures at 25 °C, 80 °C and 105 °C

Sample	TS (MPa)	EAB (%)	YM (N/m^2)
CS-25	7.61±0.94^d	122.66±11.02^a	8.81±0.61^f
CS-80	13.73±0.71^c	42.85±6.12^b	162.19±4.15^d
CS-105	15.22±2.08^c	14.04±1.78^c	170.24±9.35^c
CS1.5G-25	14.26±1.37^c	44.25±7.98^b	105.65±4.19^e
CS1.5G-80	23.02±3.23^b	6.07±2.10^d	270.24±6.76^b
CS1.5G-105	36.45±0.64^a	5.36±0.80^d	315.96±1.57^a

CS-25, CS-80, CS-105 = pure chitosan with curing at 25 °C, 80 °C and 105 °C, respectively; CS1.5G-25, CS1.5G-80 and CS1.5G-105 = chitosan crosslinked with 1.5% genipin and cured at 25 °C, 80 °C and 105 °C, respectively

Mean (± SD) values within a column superscripted with different lowercase letters are significantly ($p < 0.05$) different.

at high temperature significantly increased TS and YM while EAB slightly decreased. TS increased from 7.61 MPa (CS-25) to 13.73 MPa (CS-80) and 15.22 MPa (CS-105), while YM increased from 8.81 N/m^2 (CS-25) to 162.19 N/m^2 (CS-80) and 179.24 N/m^2 (CS-105). Similarly, with increasing curing temperature, TS of the crosslinking films increased from 14.26 MPa (CS1.5G-25) to 23.02 MPa (CS1.5G-80), while CS1.5G-105 had a maximum TS of 36.45 MPa, which was a 60% increase compared to CS-1.5G-25. YM significantly increased from 105.65 N/m^2 (CS1.5G-25) to 270.24 N/m^2 and 315.96 N/m^2 for CS1.5G-80 and CS1.5G-105, respectively. This fact could indicate that heat curing was a reinforcement of both the CS-25 and CS1.5G-25 networks. The improvement in TS and YM of the chitosan-crosslinked films after heat curing was also observed by Rivero et al. (2013), which suggested that the thermal treatment affected structural stabilization. Conventionally, when mechanical strength increases, polymer elasticity decreases. The elongation values decreased on average by 87–88% for the cured films compared to their corresponding controls (CS-25 and CS1.5G-25). A similar observation was reported by Rivero et al. (2011), where heat curing markedly reduced the flexibility of films. In the same way, Inthamat et al. (2021) reported that a declination in the segmental movement of polymer chains due to the development of the C–C double bond between genipin molecules resulted in a decrease in the elongation at break.

Morphology of thermal curing films

The surface morphologies of the CS and CS1.5G films at 25 °C, 80 °C and 105 °C are shown in Fig. 3. The film surfaces of the CS-25, CS-80 and CS-105 films (Figs. 3A–3C, respectively) were smoother than that of the CS1.5G-25 film (Fig. 3E). Increasing curing temperature increased the roughness of the CS1.5G-80 (Fig. 3F) and CS1.5G-105 (Fig. 3G) films, probably due to a rapid release of moisture on the film surface during the heat curing process (Gan et al., 2020). As shown in Figs. 3D and 3H, the cross-sectional surface of the CS-105 film was smooth. However, the CS1.5G-105 film had a dense-layered structure on the cross-sectional surface of the film, leading to improved mechanical and barrier properties of the genipin-crosslinked film.

X-ray diffractometry analysis of thermal curing films

The main objective of the XRD analysis was to observe the influence of curing temperature on the crystallinity of the CS and CS1.5G films, as shown in Fig. 1B. The X-ray diffractograms of the CS-25 film displayed two main peaks at 2θ = 8–9° and 2θ = 20–21° that were assigned to the typical crystalline forms I and II, respectively. The heat-treated CS-80 and CS-105 films had a flattening peak at 20–21°. This result further showed that heat curing affected the molecular structure of chitosan, probably relating to an increment in the number of hydrogen bonds in the chitosan

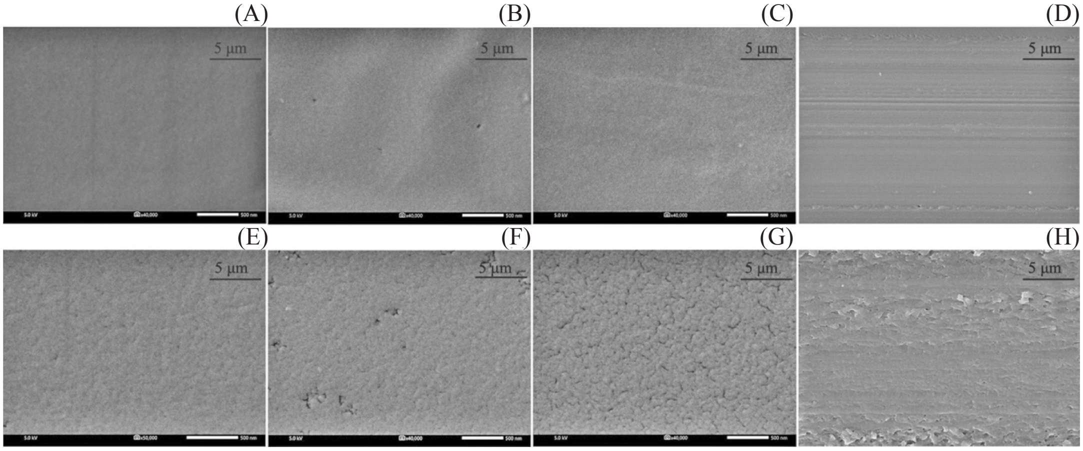

Fig. 3 Film morphology of CS and CS1.5G film surfaces with curing temperature at 25 °C, 80 °C and 105 °C: (A) CS-25; (B) CS-80; (C) CS-105; and of pure chitosan with curing at 25 °C, 80 °C and 105 °C: (E) CS1.5G-25; (F) CS1.5G-80; (G) CS1.5G-105, where chitosan is crosslinked with 1.5% genipin and cured at 25 °C, 80 °C and 105 °C, respectively; and cross-section scanning electron microspore images of: (D) CS-105; (H) CS1.5G-105

matrix (Liu et al., 2019). Furthermore, the diffractograms of the CS1.5G-80 and CS1.5G-105 films cured at different temperatures showed a broader state at the peak of 2θ = 20–21° because heat curing caused further crosslinking of the film matrix, as described by Rivero et al. (2011) and Rubentheren et al. (2016), reducing the formation of a crystalline structure.

Thermal stability of thermal curing films

Fig. 1C shows the TGA curves of the CS and CS1.5G films after curing at 25 °C, 80 °C and 105 °C. The observed first stage at 180–280 °C corresponded to an elimination of water molecules in both free and associated states in the chitosan-based film structure. The loss in the second stage at 300–380 °C was related to complex processes, such as the dehydration of the polysaccharide rings and the decomposition of units of acetylated and deacetylated chitosan (Rivero et al., 2020). However, the third stage at 571 °C, attributed to crosslinking degradation, was observed in the CS1.5G-25 film. The thermal stability levels of CS-80 and CS-105 film with curing at 80 °C and 105 °C were higher than that of the CS-25 film as shown by their slightly increasing curves. Furthermore, the curves of cured films had the highest percentage remaining mass and decomposition temperature, indicating the development of a more stable structure. In addition, this result could indicate that heat curing encouraged crosslinking reactions between chitosan and genipin.

Conclusions

An increase in the genipin concentration increased the crosslinking degree, TS and YM of the films after curing, the structure of crosslinking between chitosan and genipin was enhanced. Chitosan film crosslinked with 1.5% genipin and cured at 105 °C (CS1.5G-105) had the lowest WVP value and the most reduced hydrophilic surface. The highest TS, YM and thermal stability values were measured in the CS1.5G-105 film. Therefore, thermal curing of genipin-crosslinked chitosan improved the film properties, increasing the potential for these films to be used in food packaging applications.

Conflict of Interest

The authors declare that there are no conflicts of interest.

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