



Preparation of chitosan/curdlan/carboxymethyl cellulose blended film and its characterization

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Abstract In this study, to improve the thermal and mechanical properties of chitosan films, a chitosan/curdlan/carboxymethyl cellulose (CS/CD/CMC) ternary blended film was prepared and characterized. To prepare a uniform CS/CD/CMC ternary blended film, an effective method of blending CD with other materials was established as the following conditions: the ternary solution temperature was maintained at 60 °C, and the pH was controlled in the range from 12 to 4. Compared to the pure chitosan, the CS/CD/CMC blended films exhibited better mechanical properties, permeability, and thermal stability. In addition, visible light properties of the ternary blending film were improved. Scanning electron microscope and Fourier transform-infrared spectroscopy analyses indicated good compatibility among the CS, CD and CMC, which led to a corresponding improvement in the properties owing to interactions among the three components in the blending process. So, an effective method of blending CD with CS and CMC was established, and the blending film has good thermal and mechanical properties.

Keywords Chitosan · Curdlan · Carboxymethyl cellulose · Blending films · Properties

Introduction

In recent years, owing to the rapid development of the food industry, food packaging is facing a new revolution. Edible and degradable films have drawn considerable attention owing to severe environmental pollution caused by excessive use of synthetic polymers, based on petroleum sources (Cazón et al. 2017). There is an urgent need for industrial and academic researchers to find eco-friendly materials, such as protein, polysaccharide, cellulose, and its derivatives, to replace plastic materials (Lin and Zhao 2007). Such renewable polymers exist widely in nature and are accessible at low cost (Campos et al. 2011).

Chitosan (CS) is a kind of chitin consisting of 5000 or more amino groups linked by β -1,4 glycosidic bonds (Kumar et al. 2004). Owing to its unique biocompatibility, biodegradability, cell affinity, and antibacterial activity CS and its derivatives have shown a wide range of application in many fields, such as biomedicine, chemical, and pharmaceutical industries (Shi et al. 2006; Ciecianska 2004). In particular the antibacterial activity of CS in food preservation has drawn considerable interest. There have been many studies about the use of CS films to prolong the shelf life of meat and fruit. However, the mechanical and thermal properties of pure CS films are weak, and the films are easily broken (Haider et al. 2008). Hence, there is a need to improve CS films by blending with other materials.

Curdlan(CD) is a kind of microbial polysaccharide, composed of 1,3- β -linked D-glucose units with the formula $(C_6H_{10}O_5)_n$, and has attracted considerable attention recently (McIntosh et al. 2005; Kanke et al. 1995). CD is insoluble in most organic solvents, such as ethanol and water, but can be dissolved in alkaline aqueous solutions (pH > 12) owing to its conformational changes (Ana et al. 2014). In food applications, because of its strong heat

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stability, security, and non-toxicity, CD has been widely used as a food additive in recent years (Funami et al. 2010). Owing to its safety, biodegradation, water insolubility, and gel-like properties, CD could be considered to a polysaccharide material for edible films. However, its dissolution characteristics when blended with other materials should be solved, and there have been few reports about CD-based edible films to date. Sun et al. (2011) reported that dissolved CD in 1% sodium hydroxide and formed a mixture with CS solution, and the blended solution need to be stirred for several hours before pouring onto the film forming plate. Although the CD/CS blended films were prepared, the mechanical property required further improvements. Wu et al. (2012) prepared konjac glucomannan/CD blend films. They dissolved CD in pH 8 aqueous solution with heating at 90 °C and stirring for 3 h to form CD micro gels. These gels were then mixed with konjac glucomannan solution by stirring for another 3 h. Ahmad et al. (2015) reported gelatin/CD blended films. However, all these films were prepared at pH 12 to prepare CD blends with gelatin. Thus, the blending condition of CD with other materials requires further study.

Carboxymethyl cellulose (CMC) is a unique thickening agent that contributes to suspension stability, adhesiveness, and water retention properties, and is widely used in food, pharmaceuticals, oils, and daily chemicals (Biswal and Singh 2004). Pure CMC films are easily dissolved in pure water, such that CMC also needs to be blended with other materials for most applications (Oliveira et al. 2015). When CMC is mixed with other edible materials (such as CS, soybean protein, and polysaccharides), the mechanical strength of the blended film can be considerably improved (Sebti et al. 2003). In the present study, by controlling the temperature and adjusting the solution pH, an effective method of blending CD with other materials was established. Using this blending method, we prepared CD/CS/carboxymethyl ternary films and characterized their properties.

Materials and methods

Materials

CD was purchased from Japan's Kirin Holdings Company. CS and CMC were purchased from Shanghai Ryon Biological Technology Co. Ltd. CS's deacetylation degree was $\geq 90\%$, and its molecular weight (Mw) was 150 kDa. Other chemicals used were purchased from Nanjing Chemical Reagent Co. Ltd and all other materials were of reagent grade and were pure by analysis. Deionized water was used in this study.

Ternary film preparation

CD and CS powder were dissolved in 0.25 mol/L sodium hydroxide and 1% (v/v) lactic acid solution overnight, respectively (the final concentrations were both 20 mg/mL). The CD solution was preheated to 60 °C, and then the CS solution was added slowly into the CD solution and the pH of the mixture was adjusted to 4 with lactic acid. The CS solution and CD solution were mixed at 2:1, 1:1 and 1:2 as volume ratio. CMC were dissolved in deionized water at 60 °C, and then added into the CD/CS mixture for the final varying concentrations of 0.27%, 0.45%, 0.9%, 1.35%, and 1.8%. Continuous magnetic stirring was maintained to produce homogeneous film solutions. Then, 1.5% (v/v) of glycerin was added into the film solution as a plasticizer. Finally, the mixture was cast onto a polytetrafluoroethylene coated dish (18 cm \times 18 cm) and maintained at 60 or 90 °C for 10 min, before then being allowed to evaporate in a constant temperature and humidity chamber (25 °C, 50% RH) for 24 h.

Mechanical properties

The thickness of films was measured with a digital electronic micrometer (± 0.001 mm, Shanghai Hengju Quantitative Tools Co. Ltd). Film samples were cut into an average length of 80 mm and width of 20 mm using a double-edged razor blade. The tensile strength (TS) and elongation-at-break (EB) of the blended films were measured with a Texture Analyser (TA.XT Plus Britain Stable Micro System) with the initial grip separation and crosshead speed set to be 40 mm and 50 mm/min, respectively. All samples were tested in six parallel experiments and were equilibrated in a chamber (25 °C, RH 50%) for 24 h before testing.

Water vapor permeability

Water vapor permeability was determined according to the method of Talja et al. (2008) with a slight modification. Briefly, 20 g of desiccative CaCl_2 was placed in a 50 mL conical flask, and a height of less than 5 mm was maintained between the interface and the bottleneck. Next, the conical flask was covered with the film, and the initial weight was noted. The flasks were then placed in a chamber at 25 °C where the RH was maintained at 75%. The weights of the conical flasks were recorded every 12 h until the weight equilibrated and an average value was obtained. Each sample was tested in triplicate. The results were calculated by the following equation:

$$WVP = \frac{mL}{At\Delta p} \quad (1)$$

where m is the value of the equilibrate weight subtracting the initial weight (g); L is the film thickness (m); A is the covered film on the conical flask area (m²); t is the time of the process cost (s); Δp is the vapor pressure difference across the film (25 °C, 75% RH).

Water absorption

The water absorption was determined according to the method of Wang et al. (2007). Film samples were cut into 3 cm × 3 cm pieces and cooled to room temperature after drying in an oven and then weighed. The films were fully immersed into a beaker with a moderate amount of water at ambient room temperature for 5 h. After swelling, the films were removed from the water and excess water was wiped from the surface with filter paper until a constant weight was obtained. Each sample was tested in triplicate and the results analyzed with the relation:

$$W(\%) = \frac{M_1 - M_0}{M_0} \quad (2)$$

where M_0 is the weight of film after drying in the oven; M_1 is the constant weight of the film after wiping off excess water.

Transparency of the film

Transparency of the blended films was measured by an ultraviolet spectrophotometer method reported by Han and Floros (1997). The light transmittance of the film was measured with an ultraviolet spectrophotometer (Ultraviolet spectrophotometer, UV-2450, Shimadzu) and the wavelength of visible light was set to be 600 nm. A rectangular film of 20 cm × 50 cm was pasted on one side of the blank cuvette. The control was an empty cuvette. The transparency values of the film samples were calculated as $T = A_{600}/L$, where A_{600} and L are the light transmittance at 600 nm and the thickness of the film, respectively.

Thermal transition characteristics

The thermal transition of the film samples was analyzed by differential scanning calorimetry (DSC-60 PLUS 230V, Shimadzu, Japan). The dried samples (3–5 mg) were precisely weighed into a specified aluminum alloy crucible. An aluminum alloy crucible without samples was used as a reference. Scanning was performed under a nitrogen atmosphere with a gas flow rate of 20 mL/min. The scanning temperature range was set to be 25–300 °C with a heating rate of 10 °C/min. Thermal properties of the blending films were obtained from the scan curve.

Fourier transform-infrared characterization

Fourier transform-infrared spectroscopy (FT-IR) spectra of the selected film samples were obtained by attenuated total reflectance-Fourier transform (Nicolet IR200 FT-IR, Thermo Scientific, USA) infrared spectroscopy from KBr tablet samples (YP-2, Shanghai Shanyue Scientific Machine Lot). Briefly, the film samples were ground by the addition of liquid nitrogen and dried for 24 h at 60 °C in a vacuum drying oven. The sample was mixed with dried KBr at proportion of 1:100 (mg), and the transparent discs pressed in a tablet machine were used in the IR spectrometer the (Nexus870FT-IR). A control sample based on 100 mg of KBr was also prepared. The spectra were measured in the range of 4000–400 cm⁻¹ with automatic signal gain and collected for 32 scans at a resolution of 4 cm⁻¹. Spectral data analysis was performed with Origin 8.5 software.

Scanning electron microscopy (SEM) analysis

The morphology of the film surface was determined with a scanning electron microscope (environmental scanning electron microscope XL-30 esem, Dutch Philips Company) under 7.00 kV × 1.0 kV acceleration voltage. The selected films were cut into a 0.5 cm × 0.5 cm square using a double-edged razor blade after balancing at 60 °C for a week. The square samples were pasted on a brass stage and sprayed with gold to make the sample conductive. Images of the resulting samples were acquired at 8000 × magnification.

Statistical analyses

All experiments were measured in triplicate. Results were presented as mean values and standard deviations. Statistical analysis system (SAS, 14.0) software was used in the statistics analysis and a probability value of < 0.05 was considered to be significant. One-way of analysis variance (ANOVA) and Duncan's multiple range tests were adopted.

Results and discussion

Effects of blending condition on CS/CD film appearance

Generally, the film appearance is related to its properties, and excellent properties can be obtained from uniform, smooth films. However, it is difficult to successfully prepare blended liquid films. There are many factors that can cause agglomerates to form during the blending process,

such as the concentration of materials, the pH of the film liquid system, and the temperature of the thermal gel formation (Reddy and Rhim 2014). In this study, we investigated the effects of pH and temperature on the appearance of the CS/CD films. The appearances of CS/CD films formed under various conditions after drying are listed in Table 1. The appearance of the blended films improved as the pH was adjusted to 4. Additionally, we confirmed that the two components could be combined in equal proportions to form a smooth film without clumps, by adjusting the pH from 12 to 4, at 60 °C. The molecular mobility was enhanced at higher temperatures, resulting in better

liquidity of the mixed liquor. We could obtain uniform film solutions within a shorter time under these blending conditions compared with stirring for hours or using the homogenizer (Cozzolino et al. 2014). In subsequent experiments, all the blended films were prepared by adjusting the pH to 4 and maintaining the temperature at 60 °C.

Mechanical properties

TS (tensile strength) characterized the largest plastic deformation resistance, and reflects the fracture resistance

Table 1 Effect of pH and temperature on the appearance of blending films

Blending condition	Appearance of CS/CD films	Thickness of CS/CD films
pH 7, temperature at 25 °C	 <p>The liquidity of film liquid is poorer, cannot be evenly dispersed, the surface of film is uneven</p>	Thickness is non-uniform
pH 12, temperature controlled at 25 °C	 <p>Liquid film has a certain liquid, can be evenly dispersed, the surface of the film is smooth, but transparency is poor</p>	Thickness is uniform, ≈ 0.08 mm
pH adjusted from 12 to 7, temperature controlled at 25 °C	 <p>Liquid film of liquidity is poorer, cannot be evenly dispersed, the surface of film is uneven</p>	Thickness is non-uniform
pH adjusted from 12 to 7, temperature controlled at 60 °C	 <p>Liquid film of liquidity is poorer, cannot be evenly dispersed, the surface of film is uneven, not easy peeling the film, internal parts and hole position</p>	Thickness is non-uniform
pH adjusted from 12 to 4, temperature controlled at 60 °C	 <p>Liquid film has a certain liquid, can be evenly dispersed, the surface of the film is smooth and dry, easy peeling the film, and high transparency</p>	Thickness is uniform, ≈ 0.06 mm

of materials. The effects of the CS/CD ratio and temperature on the TS of the blended films are shown in Fig. 1a. The TS of blended film increased considerably ($p < 0.05$) as CD was added into the pure CS film and the TS value increased to a maximum of 1.9 MPa at the thermal-irreversible gel formation temperature of 90 °C, with a ratio of CS/CD = 2/1. The rise in TS was attributed to enhanced interactions (ionic and hydrogen bonding) among the CD, CS, and glycerin molecules. The plasticizer glycerin acts as a cross-linker between CS and CD. However, the TS of the blending films decreased as the content of CD was increased. The CD might weaken the interactions between the NH_3^+ groups of CS and the OH^- groups of the CD molecules (Caner et al. 1998). Furthermore, as the temperature was increased, more intense molecule movement resulted in the structure of the blending films becoming more pyknotic. Sun et al. (2011) reported a similar tendency for the tensile strength to change from addition of CS; however, in that study the TS of the CS/CD films was

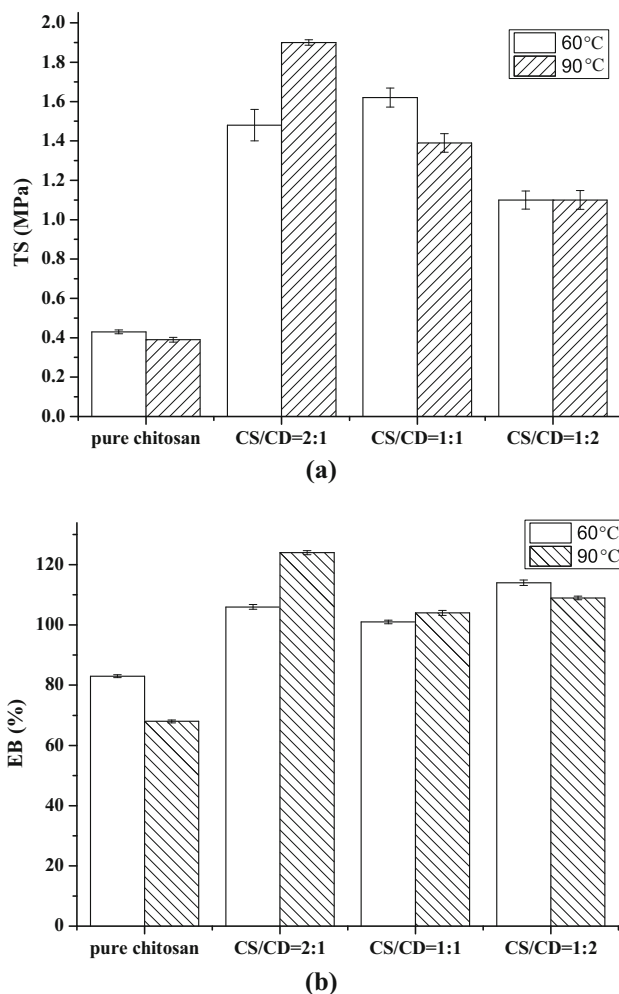


Fig. 1 Effect of CS/CD ratio and temperature on the TS (a) and EB (b) of CS/CD films

higher, which might be attributed to the lower molecular weight of the CS that we used. This result suggests that there is an optimal amount of the CD additive for reinforcing the tensile strength of the blended films. The elongation break (EB) is an indicator of the resistance degree of elastic deformation of materials. The EB results, reflecting the elasticity of the CS/CD films, are shown in Fig. 1b. Clearly, the incorporation of CD had a positive effect on the EB of the CS/CD films. The EB increased to 120% for the film casting conditions of CS/CD = 2/1, 90 °C. Because gelatin develops at higher temperature, the blending films expressed outstanding ductility. These properties could be attributed to the interactions between CS and the CD molecules (Martínez-Camacho et al. 2010). In this experiment, the CS/CD films showed good TS and EB, which were optimized at CS/CD = 2:1 and 90 °C.

The effects of the CMC concentration on the tensile strength and the elongation break of the blended films based on the optimized ratio of CS/CD and the film preparation conditions are shown in Fig. 2. The tensile strength of the film initially increased and then decreased as the concentration of CMC was increased. The TS and EB increased considerably for moderate CMC content, with the TS increasing to approximately 10.5 MPa the EB increasing to 130%. As the concentration of the CMC was increased, the solid content of the film solution was also increased, which might have increased the micromolecular network density and reinforced the probability of interactions among CS, CMC, and CD. These effects are ascribed to CS and CMC containing a large number of hydrophobic and hydrophilic groups, respectively. During the film drying, more and more intermolecular hydrogen bonds are formed and the intermolecular forces increase, thus improving the mechanical properties of the film. During the mixing process as the concentration of CMC was increased, pole-climbing phenomenon occurred and

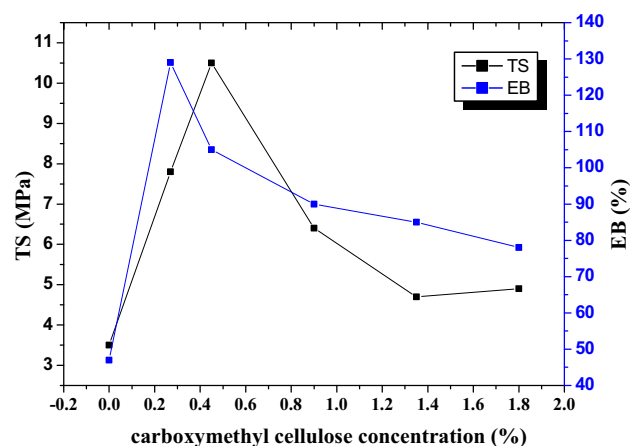


Fig. 2 Effect of CMC concentration on the TS and EB of CS/CD/CMC blending films

Table 2 Moisture content, water vapor permeability, and water absorption of pure CS, CS/CD, CS/CMC and CS/CD/CMC composite films

Film	MC (%)	WVP ($\times 10^{-10} \text{ g m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$)	WA (%)	Transparency values
Pure CS	29.98 \pm 1.73 ^a	3.65 \pm 0.098 ^c	450 \pm 8.25 ^a	4.37 \pm 0.076 ^c
CS/CD	31.25 \pm 1.66 ^a	3.58 \pm 0.066 ^b	225 \pm 5.01 ^c	4.54 \pm 0.09 ^b
CS/CMC	30.38 \pm 2.10 ^a	4.99 \pm 0.13 ^a	306 \pm 8.17 ^b	6.92 \pm 0.084 ^a
CS/CD/CMC	28.94 \pm 0.95 ^a	2.84 \pm 0.126 ^d	198 \pm 4.88 ^d	3.89 \pm 0.1 ^d

Values are given as mean \pm SD (n = 3). Different letters (a, b, c, d) in the same column means significant difference ($p < 0.05$)

stirring became difficult as the liquid film fluidity decreased. These effects resulted in poorer flow ductility and film forming ability after the liquid was transferred to the plate. Thus, the mechanical properties of the films decreased. The CMC might have induced aggregation that caused a brittle network to form in the blended films, as has been discussed in some studies (Mandal and Chakrabarty 2015; Kanmani and Rhim 2014).

Permeability

Water vapor permeability and water absorption are important properties of the films. Films with lower moisture content can allow for storage over longer times. The moisture content, water vapor permeability, and water absorption of different composite films were tested, and the results are shown in Table 2. The crystallinity, molecular size and other properties of macromolecular polymers can affect the water vapor transmission rate (WA). A higher degree of crystallinity typically leads to a lower transmission rate. The water resistance of blended films became worse as the amount of CS hydrophilic groups (NH_3^+) was increased (Ghosh et al. 2010). As shown in Table 2, the water vapor permeability of the CS/CD blending film was lower than that of the pure CS film owing to the hydrophobic chains of CD. CD itself has a unique molecular structure and is composed of a single strand and triple helix molecular stereo-structure, with a large number of hydrophobic groups (Zhang et al. 2002). When CD is mixed with CS and CMC it can help to enhance the spatial network structure of the film and improve the water resistance of the blended films. The water resistance of the CS/CD/CMC blended films was best among the different composite films tested, and its water absorption was lower than that of other composite films. It is likely that new interactions occur when the CMC is added. This might also explain the CS/CS/CMC blended film having the lowest water absorption and lowest moisture content. Therefore, as the degree of crystallization changed for the CS/CD/CMC blended films, the strength of the film structure became stronger, and the density of the structure tended to be higher. Thus, higher strength and water resistance were achieved.

The transparency of edible films is an important index for judging the sensory effect of a film. Most consumers prefer to choose more transparent packaging. Different film compositions exhibited distinct light transmission properties (Ahmad and Benjakul 2011). The transparency value of the CS/CD/CMC blended film was the lowest, as listed in Table 2. The transparency of the CS/CMC blended

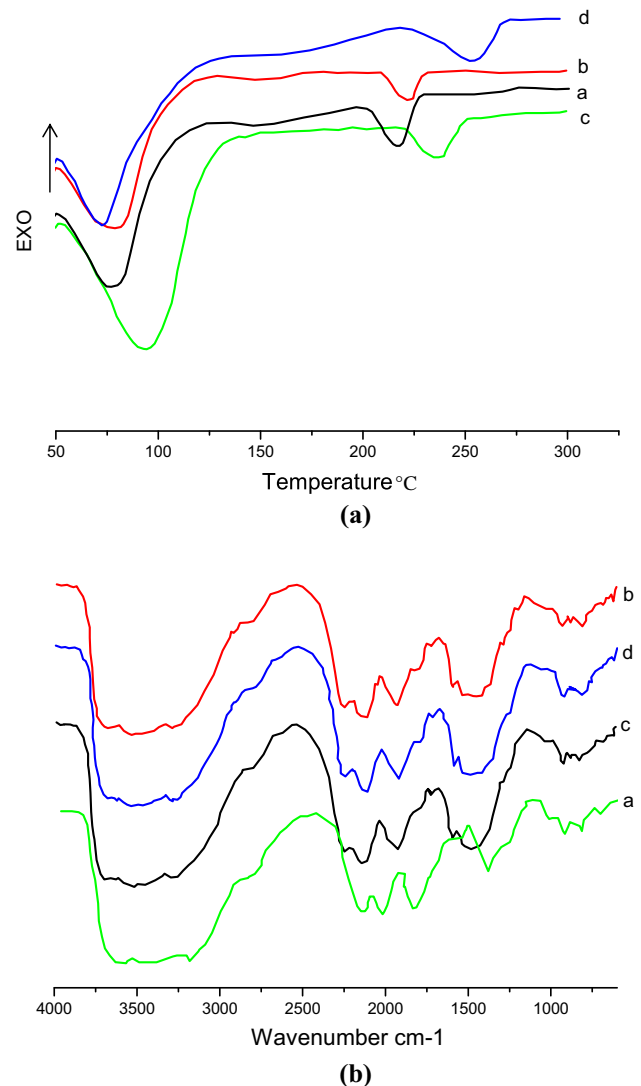
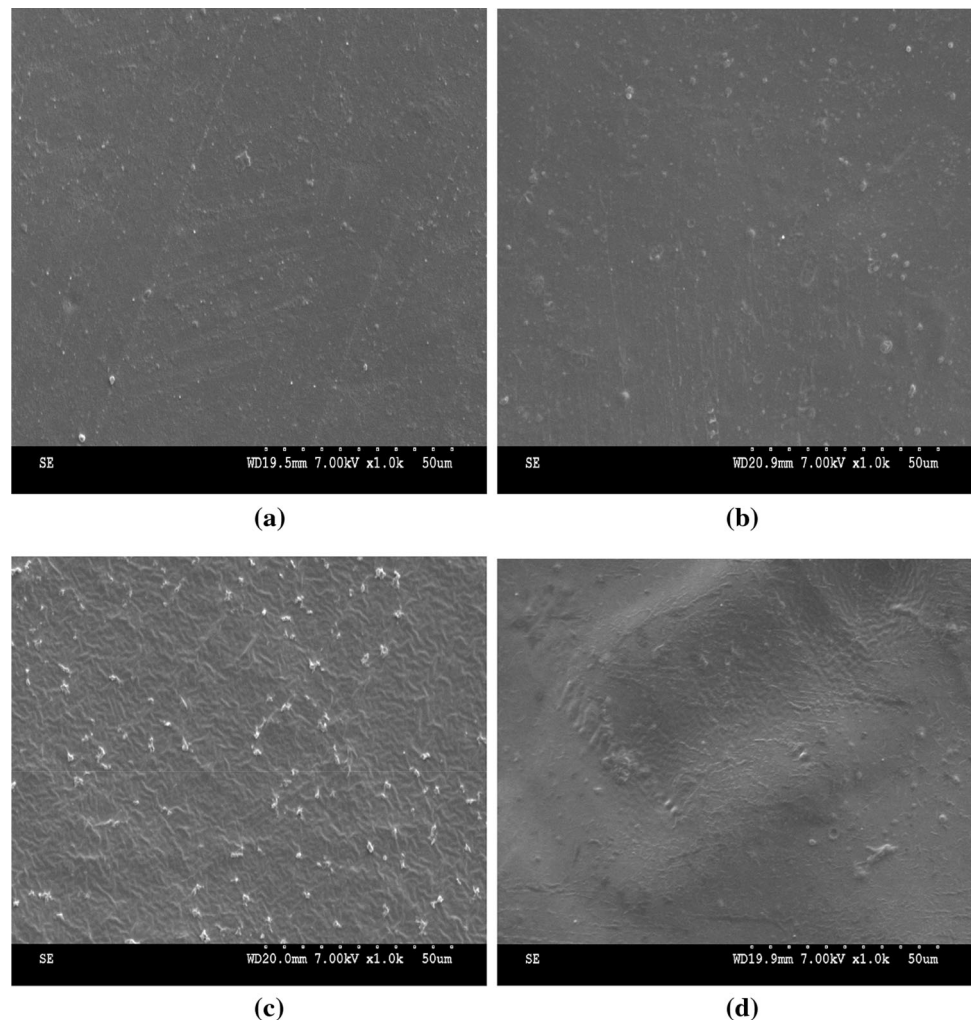


Fig. 3 DSC curves (a) and FTIR of spectra (b) of different composite films. a: pure CS; b: CS/CD; c: CS/CMC; d: CD/CS/CMC

Fig. 4 SEM micrographs of surface of different composite films. **a** pure CS; **b** CS/CD; **c** CS/CMC; **d** CS/CD/CMC



films, CS/CD blended films, and the pure CS film were higher. The more transparent films featured a higher transparency value (Ahmad et al. 2012). In conclusion, the CS/CD/CMC blending films featured low visible light transmission. Because of the relatively high degree of crystallization of CS and the good compatibility between CD, CMC, the structure of the CS/CD/CMC blending films were particularly dense. Thus, the light scattering of the blended film was greatly enhanced, and the transparency value decreased. The poor compatibility of CS and CMC led to a loose structure in the blended films and the scattering of light was not strong, resulting in a considerable increase in the transparency of the films.

Thermal transition and fourier-transform infrared characteristics

The differential scanning calorimetry (DSC) thermograms of different composite films are shown in Fig. 3a. The endothermic peak in the range of 60–90 °C was attributed

to the heat absorbed by water evaporation from the polymers, and the heat release peak of lactic acid decomposition was found to be in the range of 70–100 °C (Martínez-Camacho et al. 2010). The endothermic peak around 180–300 °C could be attributed to thermal degradation of the polymers. In the DSC curve of the pure CS film an exothermic peak appearing at 218.7 °C was attributed to debonding of the film structure or fluxing of CS with hydrogen bond breakage (Zhang et al. 2000). The DSC curves of the CS/CD, CS/CMC, and CS/CD/CMC blending films showed endothermic peaks at higher temperatures than that of the pure CS film. This finding can be explained by the interactions between the hydroxyl groups of CD and the amino groups of CS, and the ionic bond interactions between CMC and CS. The CS/CD, CS/CMC, and CS/CD/CMC blended films likely have a better thermal stability than that of the pure CS film and blending different components together is an effective method for exploring the properties of edible films. The CS/CD/CMC blended film showed a higher degradation temperature of 255.4 °C,

which implied that the CS/CD/CMC blended film was the most thermostable among the different composite films. The thermal stability of the film is related to its crystalline structure, and a decrease of thermal stability indicates weakening of the crystalline structure of the film. The blended films did not melt after heating at high-temperature for 30 min, which indicated that the films could resist high temperatures and long-term heating. These results are not shown in this paper; however, good heat resistance is important for high temperature food preservation treatments.

The interactions among the components in the blending films and the chemical bond types can be analyzed by infrared spectroscopy. The deformation vibration of the amino group in pure CS powder mainly occurs in the regions of 1645 and 1583 cm^{-1} (Gwen et al. 2007). An obvious shift of the absorption peak in the infrared spectrum of the blending films suggests the presence of interactions among CS and added substances (Zhong et al. 2011). In this experiment, pure CS film solutions were prepared by dissolving the films in lactic acid, to alter the spectrum of the pure CS film. Moreover, glycerol in the pure CS film also partially affected its spectrum. As shown in Fig. 3b, the characteristic peaks of the pure CS film mainly occurred at 1659.8 cm^{-1} (amide I, C=O bond stretching vibration) and 1571.3 cm^{-1} (amide II, N–H bond bending vibration). In addition, the peak of 3302.8 cm^{-1} was attributed to the existence of the O–H bond. In the spectra of CS/CD/CMC film, the C=O bond stretching vibration absorption peak and the position of the –OH peak shifted to a certain size. This change might be attributed to intermolecular interactions between CMC and CS. The shift of the absorption peak of the infrared spectrum can be explained by the blending of components in the films and the interactions among the various materials. These findings were also corresponding with the results of SEM and DSC analysis.

Scanning electron microscopy (SEM) analysis

We observed the surface morphology of the samples by SEM and explored the compatibility of polymer film materials. After the films dried, the microstructure of the surface was mainly related to the arrangement of the different components in the film (Pinotti et al. 2007). If several polymers have good compatibility, good stretching of the interspersed polymer suggests that the formation of the membrane will be homogeneous and dense. However, for thermodynamic reasons, molecules can separate and curl away from each other (Limpan et al. 2012). As shown in Fig. 4, the surfaces of the CS, CS/CD, and CS/CD/CMC films were smooth and the structures were compact. These results indicate that the blended film of CS, CD, and CMC

showed good compatibility, and formed a complex network structure. These findings could also be confirmed by infrared spectroscopy.

Conclusion

In the present study, we controlled temperature and solution pH to achieve an effective method of blending CS with other materials. A uniform, homogeneous CS/CD/CMC (CS/CD/CMC) ternary film was prepared through this blending method. The CS/CD/CMC blended films exhibited outstanding mechanical properties, low-permeability, and good thermal stability. SEM and FT-IR analyses indicated good compatibility between CD, CS, and CMC under the above-mentioned conditions which corresponded with improved properties. This simple approach shows promise for integrating CS/CD/CMC blended films into edible food packaging.

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Compliance with ethical standards

Conflict of interest There are no conflict to declare.

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