Effects of ultrasonic/microwave-assisted treatment on the properties of corn distarch phosphate/corn straw cellulose films and structure characterization

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Abstract Edible films were casted using aqueous solutions of corn distarch phosphate (CDP, 3 wt%) and corn straw cellulose (CSC, 0.5 wt%). The effects of ultrasonic, microwave and ultrasonic/microwave-assisted treatment on mechanical properties and light transmittance, as well as the water vapour permeability (WVP) of edible films, were evaluated. It was found that corn distarch phosphate/corn straw cellulose (CDP/CSC) films treated using ultrasonic waves/microwaves for a certain condition has a distinct increase in tensile strength, elongation at break and light transmittance and a drastic decrease in WVP. Moreover, scanning electron microscopy demonstrated that the surface and cross-section morphology of CDP/CSC films after ultrasonic/microwave-assisted treatment were smoother, denser and without a notable phase separation compared with control films. The results of mechanical properties and barrier properties were in agreement with the changes in molecular interactions detected by Fourier transform infrared spectroscopy and X-ray diffraction analysis. These findings indicate that ultrasonic/microwave-assisted treatment can improve the application of biodegradable films.

Keywords Ultrasonic/microwave-assisted treatment · Corn distarch phosphate · Corn straw cellulose · Films

Introduction

Recently, natural biological materials research has gained considerable importance in the food packaging industry because the materials are non-toxic, harmless, biodegradable, and environmentally friendly (Eca et al. 2015; Espitia et al. 2014). As a natural biopolymer, starch is supposed to be an environmentally friendly, renewable, low cost resource that is readily available (Shankar and Rhim 2016). Starch-based films have been studied earlier, including their components, processes, equipment, and properties, and their applications have been carried out extensively; moreover, a series of progresses has been made (Jiang et al. 2016). Edible films have to have a certain mechanical strength and the ability to control moisture, oxygen, and aroma components transferred between food and the surrounding environment (Nisa et al. 2015). A previous study showed that fruits and vegetables are packaged by using edible films, with the quality of the final product quality being improved and shelf life being extended, providing convenience to consumers for consumption (Lago-Vanzela et al. 2013; Sousa et al. 2016). However, the physical properties of starch are worse than those of synthetic polymers, and the starch-based films have some drawbacks, such as poor barrier and stability, leading to packaged product exposure to the environment and spoilage (Kuorwel et al. 2013). Fortunately, these properties can be improved using physical, chemical and enzyme modification methods. For instance, edible films of konjac glucomannan are treated using acid, with their water adsorption capacity and water vapour permeability being significantly

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increased compared with untreated ones (Cheng et al. 2007). Moreover, it has been reported that gamma irradiation is an efficient way to modify the properties of konjac glucomannan and chitosan blend films, the tensile strength being enhanced by 40% and the breaking elongation being enhanced by 30% (Li et al. 2011).

Corn distarch phosphate (CDP) uses corn starch as the raw material, with phosphate groups with anionic property being introduced to the molecular structure (Li et al. 2010). Compared with corn starch, the functional properties of this bio-polymer are obviously changed, with the positive results of this modification consisting of improved stability and transparency and reduced pasting temperature (Bidzinska et al. 2012). CDP-based films have higher strength and toughness.

Additionally, cellulose has been added to improve the mechanical properties and barrier properties (Dias et al. 2011). Among them, corn straw cellulose (CSC) can be widely studied because it is an abundant resource, cheap, nontoxic, and safe (Li et al. 2013). Nevertheless, the strong intermolecular hydrogen bonds in natural cellulose make it difficult to dissolve in common solvents, and the application of cellulose for edible films is limited (Wu et al. 2016).

Furthermore, improvement of the performance of edible film via ultrasonic treatment has been demonstrated, e.g., enhanced intermolecular forces, formation of a dense structure, elimination of air bubbles and easy vacuum degassing (Wang et al. 2014b). Microwaves offer a fast and convenient method for heating, resulting in the breakage of hydrogen bonds and strengthening of the intermolecular crosslinking interactions (Jacquot et al. 2014). Currently, ultrasonic/microwave-assisted treatment is widely used in the extraction and synthesis of components, the advantages of the proposed method being high extraction efficiency and solvent-free extraction (Feng et al. 2014), and rarely used to improve the performance of protein edible film (Wang et al. 2014b). However, the study of ultrasonic/microwave-assisted treatment on CDP/CSC films has not been reported.

The objective of this study was to produce CDP/CSC films and study the effect of ultrasonic/microwave-assisted treatment on the properties and structure characterization. The properties included mechanical properties, light transmittance and WVP. The structure characterization, such as the surface and cross-section morphology, the existence and interaction of CDP and CSC, and the crystallization of CDP/CSC films, was analysed. Moreover, the microstructures of the films were investigated to provide deeper insight into the mechanical properties and barrier properties.

Materials and methods

Materials

CDP was purchased from Dahua Starch Co., Ltd. (Changchun, China). CSC was made in the laboratory. Carboxymethyl cellulose (CMC, 800–1200 mPa s) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Glycerol (Gly, $\text{CH}_8\text{O}_3 \geq 99\%$) was supplied by Yongda Chemical Reagent Co., Ltd. (Tianjin, China).

Preparation of CSC

Dried corn straw was crushed by using an ultra-micro pulveriser (LWF-6B1, Jinan Longwei Pharmaceutical Equipment Co., Ltd., Jinan, China), and the powder was sieved through a 300-mesh screen. 10 g corn straw powder was mixed with 200 mL distilled water at 90 °C for 1 h. Furthermore, the water-soluble free samples were delignified using 5% (w/v) sodium chlorite at pH 3.0–4.0 and adjusted using 10% (w/v) glacial acetic acid solution at 80 °C for 3 h. Finally, the holocellulose was extracted using 6% (w/v) sodium hydroxide at 70 °C for 5 h (Li et al. 2013). After filtration, the residues were washed to neutral, using 75% ethanol and distilled water, and freeze-dried into powder using a vacuum freeze-drying machine (LGJ-50FD, Henan Brothers Equipment Co., Ltd., Henan, China) (Moran et al. 2008).

Preparation of CDP/CSC films

Starch films were typically prepared by drying thin layers of cast film-forming solutions (Sun et al. 2016; Thakhiw et al. 2014). The casts of CDP/CSC films were prepared via a water evaporation method. The solution of CDP (3 wt%) was gelatinized at 68 °C for 25 min. Furthermore, CSC (0.5 wt%), Gly (1.0%, wt%) and CMC (0.8%, wt%) were added to the CDP solution. The mixture was magnetically stirred at room temperature for 20 min, and the air bubbles in the mixture were removed by vacuum degassing (Peressini et al. 2003). A volume of 100 mL of the CDP/CSC films solution was modified by using a microwave and ultrasonic combination reaction system (SL-SM50, Nanjing Shunliu Instruments Co., Ltd, Nanjing, China). The films were coded as MxUy. Film codes and details of the conditions of ultrasonic/microwave-assisted treatment on CDP/CSC films are shown in Table 1. Then, the CDP/CSC films solution was poured uniformly into a square film applicator of Plexiglas (20 × 20 cm), and dried at 60 °C for 5 h. The CDP/CSC films were peeled after being placed into constant temperature and humidity equipment (SPX-

Table 1 The conditions of ultrasonic/microwave-assisted treatment

Treatment no.	Microwave power (W)	Ultrasonic power (W)	Thickness (mm)
M0U0 (control)	0	0	0.1086 ± 0.0018 ^{abc}
M0U180	0	180	0.1076 ± 0.0024 ^{abcd}
M0U360	0	360	0.1052 ± 0.0023 ^{abcd}
M0U540	0	540	0.1108 ± 0.0022 ^a
M0U720	0	720	0.1054 ± 0.0024 ^{abcd}
M75U0	75	0	0.1094 ± 0.0040 ^{ab}
M75U180	75	180	0.1066 ± 0.0023 ^{abcd}
M75U360	75	360	0.1094 ± 0.0045 ^{ab}
M75U540	75	540	0.1072 ± 0.0017 ^{abcd}
M75U720	75	720	0.1094 ± 0.0044 ^{ab}
M150U0	150	0	0.1068 ± 0.0026 ^{abcd}
M150U180	150	180	0.1070 ± 0.0025 ^{abcd}
M150U360	150	360	0.1092 ± 0.0034 ^{abc}
M150U540	150	540	0.1060 ± 0.0027 ^{abcd}
M150U720	150	720	0.1078 ± 0.0037 ^{abcd}
M225U0	225	0	0.1086 ± 0.0057 ^{abc}
M225U180	225	180	0.1040 ± 0.0045 ^{bcd}
M225U360	225	360	0.1054 ± 0.0046 ^{abcd}
M225U540	225	540	0.1044 ± 0.0054 ^{bcd}
M225U720	225	720	0.1056 ± 0.0027 ^{abcd}
M300U0	300	0	0.1038 ± 0.0034 ^{bcd}
M300U180	300	180	0.1068 ± 0.0056 ^{abcd}
M300U360	300	360	0.1066 ± 0.0062 ^{abcd}
M300U540	300	540	0.1026 ± 0.0038 ^d
M300U720	300	720	0.1034 ± 0.0046 ^{cd}

^{a,b,c,d,e}For each measurement, the data marked by different letters in a column indicate significant difference ($p < 0.05$)

250, Changzhou Noki Instruments Co., Ltd, Changzhou, China) at 25 ± 1 °C and 60% relative humidity for 24 h.

Thickness measurements

Thickness of CDP/CSC films were measured using digital micrometer (E0571, Endura Greenlee tools Co., Ltd, Shanghai, China) at five random points for each film. The average with an accuracy of 0.001 mm was calculated for mechanical properties and water vapor permeability.

Mechanical properties

The CDP/CSC films were cut into a rectangular shape, with a length of 70 mm and width of 25 mm. TS and EAB were used to evaluate the mechanical properties of the CDP/CSC films at 25 ± 1 °C using a texture analyser (CT-3, Brookfield engineer laboratories, INC., USA). A texture analysis—dual grip assembly (TA-DGA) stainless steel fixture was used to measure force in tension mode, depicting the force-distance plot of the CDP/CSC films (Villarruel et al. 2015). Measurement settings were target

value – 20 mm, target load – 0.05 MPa, and test speed – 0.5 mm s^{-1} . The fracture occurred approximately at the sample center, and an average value of at least three replicates for each film was taken. TS was calculated by dividing the maximum force by the cross sectional area of the film using Eq. (1). EAB was expressed as percentage of change in the initial length of the film between grips at break using Eq. (2) (Fan et al. 2016).

$$TS = \frac{F}{B \times T} \quad (1)$$

$$EAB = \frac{D - L}{L} \times 100\% \quad (2)$$

where F is the maximum tension at break (N); B is the width of the film (mm); T is the thickness of the film (mm); D is the distance at break (mm); L is the length of the test (mm).

Light transmittance

Light transmittance of the films was measured by using a UV–Vis spectrophotometer (UV-2600, Shimadzu Suzhou

Instruments Mfg. Co, Ltd). The CDP/CSC films were cut into a rectangular shape (40 mm × 10 mm). A blank cuvette was used as the control, with the sample close to the inside of the cuvette. The light transmittance was measured at a wavelength of 550 nm.

Water vapour permeability (WVP)

Water vapour permeability (WVP, $\times 10^{-12}$ g cm⁻¹ s⁻¹ - Pa⁻¹) tests were conducted based on the modification of ASTM standard method E96-95 using a specially designed permeation cell that was maintained at 25 °C and 95% relative humidity (RH), as described in previous works (Ortega-Toro et al. 2015). Each test cup [50 mm (diameter) × 30 mm (depth)] was covered with a circular film sample, which was used to accomplish the test. The water vapour transmission rate (WVTR) was calculated by measuring the reduction weight of distilled water as time passed using Eq. (3), and WVP was calculated using Eq. (4) (Benbettaieb et al. 2014).

$$WVTR = \frac{1}{A} \left(\frac{\Delta m}{t} \right) \quad (3)$$

$$WVP = \frac{WVTR \times T}{P_1 - P_2} \times 100\% \quad (4)$$

where A is the area of the permeability cups (cm²), Δm is the weight change of the permeability cups (g), t is the time (s), T is the thickness of the film sample (mm), P_1 is the water vapour pressure outside the film sample at 25 °C (Pa), and P_2 is the water vapour pressure inside the film sample at 25 °C (Pa).

Scanning electron microscopy (SEM)

The surface and cross-section morphology of the CDP/CSC films were observed by using a cold field emission scanning electron microscope (S-3000N, Japan Electronics Co., Ltd., Japan). The CDP/CSC films were cut into two sizes: one was square-shaped (5 mm × 5 mm), while the other was rectangular-shaped (5 mm × 1 mm). Samples were fixed onto different sample platforms using double-sided adhesive tape and sputtered with a thin layer of gold. Under the condition of accelerating voltage 20 kV, all samples were observed and the surface and cross-section morphology of the CDP/CSC films were photographed.

Fourier transform infrared spectroscopy analysis (FT-IR)

FT-IR spectra of the CDP/CSC films were analysed via Fourier transform infrared spectroscopy (IS50, Thermo Nicolet Corporation, American) in the range of

550–4000 cm⁻¹, with a resolution of 4 cm⁻¹ and number of scans equal to 16.

X-ray diffraction (XRD)

The crystalline phases of the CDP/CSC films were recorded using an X-ray diffractometer (DX-2700 XRD, Haoyuan Instrument Co., Ltd., China) with a Cu target. All the CDP/CSC films samples were cut into 20 mm squares. Measurement settings were stepping measurement, tube voltage – 40 kV, tube current – 40 mA, scanning range – 5° to 50°, step angle – 0.020, sampling time – 0.1 s.

Statistical analysis

Data of the research was reported as the mean of a triplicate. The analysis of variance (SPSS for Windows, version 19) and Duncan's multiple range tests were performed to detect significant differences in film properties. The significance level used was 0.05.

Results and discussion

Mechanical properties

TS and EAB are important textural parameters for films, enabling them to maintain their integrity and withstand external stress. The effects of ultrasonic/microwave-assisted treatment on the mechanical properties of CDP/CSC films are depicted in Fig. 1. As seen in Fig. 1, TS and EAB of the control films were 19.75 MPa and 46.89%, respectively. The continuous increase in TS of CDP/CSC films occurred upon increasing ultrasonic power, and TS increased to a maximum (28.04 MPa) at ultrasonic power of 720 W. Compared with control films, there was about 41.97% enhancement in TS value. The ultrasonic treatment might lead to conformational changes, facilitating the interaction between polymers, and might be favourable to constructing more compact and tighter film. This improved film microstructure might also be an important factor for TS enhancement. Furthermore, the chain was destroyed, thus releasing amylose after ultrasonic treatment and higher amylose content in the casting solution has been shown to produce stronger films, as has been confirmed (Fan et al. 2014; Tharanathan 2003). As can also be observed in Fig. 1b, as ultrasonic power increased, EAB increased initially before decreasing. Here, appropriate ultrasonic power could improve EAB, but too high ultrasonic power might lead to the formation of a dense mesh structure due to high intermolecular hydrogen bonds between polymers; therefore flexibility declined, which could cause a decrease in EAB (Cheng et al. 2010).

Fig. 1 Effects of ultrasonic/microwave-assisted treatment on the mechanical properties TS (a) and EAB (b) of CDP/CSC films. Different letters for each treatment show significant difference ($p < 0.05$)

TS reached the maximum (33.63 MPa) at ultrasonic power of 720 W and microwave power of 150 W, which was presented in Fig. 1a. And as shown in Fig. 1b, at constant microwave power (75, 150 and 225 W), EAB of CDP/CSC films first increased and then decreased with increasing ultrasonic power. Ultrasonic power of 540 W and microwave power of 225 W resulted in the maximum EAB (80.39%) which was much higher than the value of 46.89% that control films. In previous studies, it was revealed that ultrasonic/microwave-assisted treatment could reduce particles' sizes and enlarge particles' surface areas, enhancing the interaction of particles in a matrix (de Moura et al. 2009). Furthermore, ultrasonic/microwave could promote the integration of blends, modify the molecular structure of the polymer network, and enhance the intermolecular force. In contrast, ultrasonic/microwave-assisted treatment could also reduce intermolecular spacing and the mobility of polymeric chains (Wang et al. 2014b). When the microwave power was fixed at

300 W, EAB exhibited a continuous decrease with increasing ultrasonic power. This was because higher ultrasonic and microwave power could produce more heat energy, provoke structural discontinuities, and reduce cohesion forces, causing fracture of the film, resulting in decreased EAB. Similar phenomenon occurred in soy protein isolate/titanium dioxide films (Wang et al. 2014a). Regardless, the TS and EAB of CDP/CSC films were improved significantly by the suitable ultrasonic/microwave-assisted treatment.

Light transmittance

The effects of ultrasonic/microwave-assisted treatment on the light transmittance of CDP/CSC films are shown in Fig. 2. Light transmittance can be used to evaluate the compatibility of different polymers; the light transmittance will be reduced when the compatibility of a polymer is poor. When incident light strikes an interface, light might

spread in different ways, such as through reflection, transmission, refraction, scattering or absorption (Wu et al. 2012). As shown in Fig. 2, the light transmittance could be improved under suitable conditions of ultrasonic power and microwave power. Under microwave power of 0 W, the light transmittance increased with increasing ultrasonic power probably because the chemical bonds in the film solution were broken by ultrasonic cavitation and the particle sizes became smaller (Cheng et al. 2010). Meanwhile, the mixed solutions of films were degassed under ultrasonic treatment, reducing the loss of light reflectance at the interfaces (Cai et al. 2016). With increasing microwave power, the light transmittance increased at first and then decreased. The film solution was made more uniform via the method of appropriate microwave heating; as the surfaces of CDP/CSC films were made more uniform and smooth, light transmittance was increased. Furthermore, the compatibility of CDP and CSC was improved via ultrasonic/microwave-assisted treatment. The light transmittance of CDP/CSC films reached 66.12% under ultrasonic power of 540 W and microwave power of 225 W, which was 23.90% higher in comparison with control films. These indicated that the ultrasonic power and microwave power had a significant effect on the light transmittance, compared with the control films ($p < 0.05$).

Water vapour permeability (WVP)

WVP is related to molecular aggregation structure, diffusion rate and solubility of water in the film (Nafchi et al. 2017). As Fig. 3 shows, ultrasonic power and microwave power had a significant impact on WVP. The higher ultrasonic power and microwave power could contribute to decrease WVP of CDP/CSC films, leading to a minimum ($0.6098 \times 10^{-12} \text{ g cm}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$) at ultrasonic power of 540 W and microwave power of 300 W. This was due to

the molecular aggregation structure and compactness of CDP/CSC films being improved by the ultrasonic/microwave-assisted treatment. At the same time, this suggested that the intermolecular forces of CDP were increased, the arrangement of polymers transitions from not oriented to oriented, and the molecular structure of CDP/CSC films was changed, leading to the increase of moisture barrier properties. The action site between the molecules will not continue to be exposed when the ultrasonic power and microwave power increase to a certain level, and the oriented network structure between molecules will be disrupted once again, water blocking performance of CDP/CSC films will be reduced, and WVP of CDP/CSC films will not continue to decrease.

Scanning electron microscopy (SEM)

The dispersion state of the film components and binding of the phase interface can be presented clearly via SEM (Nagarajan et al. 2015). The surfaces of films are smooth and flat, suggesting that the compatibility of the polymer is good (Nagarajan et al. 2015). On the contrary, spherical particles will be exposed on the surface films and the phase interface will be significant. The differences in the surface and cross-section morphology of CDP/CSC films can be observed in Fig. 4. The results showed that the surfaces of CDP/CSC films were rough and the cross-sections of CDP/CSC films were loose without ultrasonic and microwave treatment. The surfaces and cross-sections of CDP/CSC films treated by using only microwave or ultrasonic treatment were smooth and dense, and the effects of microwave treatment were not as good as those of ultrasonic treatment. The effect of ultrasonic/microwave-assisted treatment was the best: the surfaces of CDP/CSC films became very smooth and homogeneous, forming a compact arrangement of polymer chains, and the cross-sections of CDP/CSC

Fig. 2 Effects of ultrasonic/microwave-assisted treatment on the light transmittance of CDP/CSC films. Different letters for each treatment show significant difference ($p < 0.05$)

Fig. 3 Effects of ultrasonic/microwave-assisted treatment on the water vapour permeability of CDP/CSC films. Different letters for each treatment show significant difference ($p < 0.05$)

films became very dense, with no obvious separation in the phase interface. This suggested that molecules between CDP and CSC form crosslinking, which was beneficial to improving the compatibility of the polymer. Similar phenomena were observed by other authors in methylcellulose/stearic acid blending films and corn starch films (Ortega-Toro et al. 2014; Zhong et al. 2015).

Fourier transform infrared spectroscopy analysis (FT-IR)

In general, no functional group is generated or disappears when two or more materials are mixed, mainly due to the changes of non-covalent bonds or some secondary bonds (Li et al. 2015; Villarruel et al. 2015). The chemical structure of CDP/CSC films investigated by using FTIR is presented in Fig. 5. The absorption peak at $3500\text{--}3200\text{ cm}^{-1}$ was due to the stretching vibration of the O–H bond and N–H bond; the O–H absorption band is broadened and shifts to the lower absorption band via ultrasonic/microwave-assisted treatment. The absorption peaks approximately 2923 cm^{-1} were due to the stretching vibration of the saturated C–H bond. The absorption peak approximately 1714 cm^{-1} was due to the stretching vibration of the C=O bond; the absorption peak was shifted higher due to the ultrasonic/microwave-assisted treatment, with the results indicating that the force constant of the C=O bond increases and the bond length was shorter. The absorption peaks approximately 1589, 1334 and 1233 cm^{-1} assigned to the N–H bending (amide II) bands and C–N stretch of amide III, respectively. These data indicated that the intermolecular hydrogen bond interactions were strengthened and compatibility was improved. The absorption peak approximately 1154 cm^{-1} was due to the stretching vibration of the C–C bond, while the

absorption peaks approximately 1073 and 994 cm^{-1} were due to the stretching vibration of the C–O bond, that belong to the glucosidic bond of the sugar as it has been also observed by Alarcon-Moyano et al. (2017) in edible films. In general, positions and intensities of the peak can expressed the degree of order and conformation in the system. Earlier studies demonstrated that FTIR may be used to infer crystallinity as short-range technique (Singh et al. 2009). Compared with the control, the absorption peak of the stretching vibration of the C=O bond and stretching vibration of the C–O bond due to ultrasonic/microwave-assisted treatment was blue-shifted, while the peak of the O–H bond changes significantly. Likewise, small shifts in some peaks could be detected for ultrasonic/microwave-assisted treatment films compared to the corresponding bands of the control films. These changes suggested that some changes in molecular interactions inside the starch matrix occurred, associated with the diffusion of compounds added at the interface; the results were in agreement with earlier reports (Ortega-Toro et al. 2015).

X-ray diffraction (XRD)

Figure 6 shows XRD spectra of the CDP/CSC films with and without ultrasonic and microwave-assisted treatment. As shown in Fig. 6, the typical peaks of control films were at 2θ of approximately 17.1° and 22.7° , and there was no strong crystalline form. These indicated that the control films were in an amorphous state and had some weak peaks of type B crystals. Sanyang et al. (2016) reported that the amylose within the starch is mainly responsible for the crystallinity of starch based films. The reason for this phenomenon might be due to water and glycerol infiltrate the interior of CDP, the establishment of stable single chain

Fig. 4 SEM of CDP/CSC films: **a** the surface of the control (M0U0), **b** the cross-section of the control (M0U0), **c** the surface of microwave treatment (M300U0), **d** the cross-section of microwave treatment (M300U0), **e** the surface of ultrasonic treatment (M0U540), **f** the

cross-section of ultrasonic treatment (M0U540), **g** the surface of ultrasonic/microwave-assisted treatment (M225U720), **h** the cross-section of ultrasonic/microwave-assisted treatment (M225U720)

conformations helices were formed and the double helix conformations was disrupted (Zhong and Li 2014). Ninago et al. (2015) also reported similar results regarding the

effect of glycerol on the crystallinity of starch films. Furthermore, starch gelatinization and retrogradation lead to the crystalline structure is disorganized during heating, and

Fig. 5 FT-IR spectra of CDP/CSC films: **a** control (M0U0), **b** microwave treatment (M300U0), **c** ultrasonic treatment (M0U540), **d** ultrasonic/microwave-assisted treatment (M225U720)

Fig. 6 XRD spectra of CDP/CSC films: **a** control (M0U0), **b** microwave treatment (M300U0), **c** ultrasonic treatment (M0U540), **d** ultrasonic/microwave-assisted treatment (M225U720)

the films presented relatively low crystallinity (Singh et al. 2009).

There was a perceptible change in the peak intensity of ultrasonic and microwave-assisted treatment films in comparison with the control films. The typical peaks of CDP/CSC films after ultrasonic and microwave-assisted treatment were shown to be at 2θ of approximately 17.1° , 19.5° and 22.7° , and it was important to note that intensity of peaks is markedly enhanced. Observed changes could be explained by considering that strong intermolecular interactions between CDP and CSC were generated by ultrasonic and microwave-assisted treatment and that the individual components of the CDP/CSC films had better compatibility. Previous research has revealed that film crystallinity is highly related to chain mobility, and film properties will be improved when enhance starch solubilization and chain mobility by ultrasonic treatment (Liu and Han 2005). Similar trends were reported by Cheng et al. (2010) for the properties of starch film when working with ultrasonic treatment. Furthermore, this suggested that high intensity ultrasonic treatment was favourable to the formation of films with excellent properties.

Conclusion

The corn distarch phosphate/corn straw cellulose (CDP/CSC) films were prepared using ultrasonic/microwave-assisted treatment. The mechanical properties, light transmittance and water vapour permeability (WVP) of films were evaluated, which were desirable for the food industry. These properties could offer several advantages to the fresh food such as improvement in the retention of color, water and flavor components, the maintenance of quality during shipping and storage, the reduction of storage disorders and improved consumer appeal. The experiments indicated that the intensification of ultrasonic/microwave power had a significant effect on the tensile strength (TS) and elongation at break (EAB) of the resulting films as well as the microstructure. Moreover, results showed that light transmittance and water vapour permeability by ultrasonic/microwave-assisted treatment were more advantageous than the control films due to the better molecular aggregation structure and appearance.

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References

Alarcon-Moyano JK, Bustos RO, Lidia Herrera M, Matiacevich SB (2017) Alginate edible films containing microencapsulated

lemongrass oil or citral: effect of encapsulating agent and storage time on physical and antimicrobial properties. *J Food Sci Technol Mysore* 54:2878–2889. <https://doi.org/10.1007/s13197-017-2726-1>

- Benbettaieb N, Kurek M, Bornaz S, Debeaufort F (2014) Barrier, structural and mechanical properties of bovine gelatin–chitosan blend films related to biopolymer interactions. *J Sci Food Agric* 94:2409–2419. <https://doi.org/10.1002/jsfa.6570>
- Bidzinska E et al (2012) Effect of phosphorylation of the maize starch on thermal generation of stable and short-living radicals. *Starch-Starke* 64:729–739. <https://doi.org/10.1002/star.201100206>
- Cai J et al (2016) Well-aligned cellulose nanofiber-reinforced polyvinyl alcohol composite film: mechanical and optical properties. *Carbohydr Polym* 140:238–245. <https://doi.org/10.1016/j.carbpol.2015.12.039>
- Cheng LH, Abd Karim A, Seow CC (2007) Effects of acid modification on physical properties of konjac glucomannan (KGM) films. *Food Chem* 103:994–1002. <https://doi.org/10.1016/j.foodchem.2006.09.052>
- Cheng WJ, Chen JC, Liu DH, Ye XQ, Ke FS (2010) Impact of ultrasonic treatment on properties of starch film-forming dispersion and the resulting films. *Carbohydr Polym* 81:707–711. <https://doi.org/10.1016/j.carbpol.2010.03.043>
- de Moura MR, Aouada FA, Avena-Bustillos RJ, McHugh TH, Krochta JM, Mattoso LHC (2009) Improved barrier and mechanical properties of novel hydroxypropyl methylcellulose edible films with chitosan/tripolyphosphate nanoparticles. *J Food Eng* 92:448–453. <https://doi.org/10.1016/j.jfoodeng.2008.12.015>
- Dias AB, Muller CMO, Larotonda FDS, Laurindo JB (2011) Mechanical and barrier properties of composite films based on rice flour and cellulose fibers. *LWT Food Sci Technol* 44:535–542. <https://doi.org/10.1016/j.lwt.2010.07.006>
- Eca KS, Machado MTC, Hubinger MD, Menegalli FC (2015) Development of active films from pectin and fruit extracts: light protection, antioxidant capacity, and compounds stability. *J Food Sci* 80:C2389–C2396. <https://doi.org/10.1111/1750-3841.13074>
- Espitia PJP, Du WX, Avena-Bustillos RD, Soares NDF, McHugh TH (2014) Edible films from pectin: physical–mechanical and antimicrobial properties—a review. *Food Hydrocoll* 35:287–296. <https://doi.org/10.1016/j.foodhyd.2013.06.005>
- Fan JM, Ma W, Liu GQ, Yin SW, Tang CH, Yang XQ (2014) Preparation and characterization of kidney bean protein isolate (KPI)–chitosan (CH) composite films prepared by ultrasonic pretreatment. *Food Hydrocoll* 36:60–69. <https://doi.org/10.1016/j.foodhyd.2013.08.024>
- Fan H, Ji N, Zhao M, Xiong L, Sun Q (2016) Characterization of starch films impregnated with starch nanoparticles prepared by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation. *Food Chem* 192:865–872. <https://doi.org/10.1016/j.foodchem.2015.07.093>
- Feng XF, Jing N, Li ZG, Wei D, Lee MR (2014) Ultrasound-microwave hybrid-assisted extraction coupled to headspace solid-phase microextraction for fast analysis of essential oil in dry traditional Chinese medicine by GC–MS. *Chromatographia* 77:619–628. <https://doi.org/10.1007/s10337-014-2642-8>
- Jacquot C, Jacquot M, Marques P, Jasiewicz J, Akhtar MJ, Didelot AS, Desobry S (2014) Influence of microwave heating time on the structure and properties of chitosan films. *J Appl Polym Sci*. <https://doi.org/10.1002/App.40779>
- Jiang SS, Liu CZ, Wang XJ, Xiong L, Sun QJ (2016) Physicochemical properties of starch nanocomposite films enhanced by self-assembled potato starch nanoparticles. *LWT Food Sci Technol* 69:251–257. <https://doi.org/10.1016/j.lwt.2016.01.053>
- Kuorwel KK, Cran MJ, Sonneveld K, Miltz J, Bigger SW (2013) Water sorption and physicochemical properties of corn starch-

- based films. *J Appl Polym Sci* 128:530–536. <https://doi.org/10.1002/app.38213>
- Lago-Vanzela ES, do Nascimento P, Fontes EAF, Mauro MA, Kimura M (2013) Edible coatings from native and modified starches retain carotenoids in pumpkin during drying. *LWT Food Sci Technol* 50:420–425. <https://doi.org/10.1016/j.lwt.2012.09.003>
- Li GL, Zhang JH, Zeng J, Gao HY (2010) Optimization of preparation of corn starch phosphates by response surface methodology. *Modell Simul* 1:51–55
- Li B, Li J, Xia J, Kennedy JF, Yie X, Liu TG (2011) Effect of gamma irradiation on the condensed state structure and mechanical properties of konjac glucomannan/chitosan blend films. *Carbohydr Polym* 83:44–51. <https://doi.org/10.1016/j.carbpol.2010.07.017>
- Li D, Zhu FZ, Li JY, Na P, Wang N (2013) Preparation and characterization of cellulose fibers from corn straw as natural oil sorbents. *Ind Eng Chem Res* 52:516–524. <https://doi.org/10.1021/ie302288k>
- Li J, Ye FY, Liu J, Zhao GH (2015) Effects of octenylsuccination on physical, mechanical and moisture-proof properties of stretchable sweet potato starch film. *Food Hydrocoll* 46:226–232. <https://doi.org/10.1016/j.foodhyd.2014.12.017>
- Liu Z, Han JH (2005) Film-forming characteristics of starches. *J Food Sci* 70:E31–E36
- Moran JI, Alvarez VA, Cyras VP, Vazquez A (2008) Extraction of cellulose and preparation of nanocellulose from sisal fibers. *Cellulose* 15:149–159. <https://doi.org/10.1007/s10570-007-9145-9>
- Nafchi AM, Olfat A, Bagheri M, Nouri L, Karim AA, Ariffin F (2017) Preparation and characterization of a novel edible film based on *Alyssum homolocarpum* seed gum. *J Food Sci Technol Mysore* 54:1703–1710. <https://doi.org/10.1007/s13197-017-2602-z>
- Nagarajan M, Benjakul S, Prodpran T, Songtipya P (2015) Properties and characteristics of nanocomposite films from tilapia skin gelatin incorporated with ethanolic extract from coconut husk. *J Food Sci Technol Mysore* 52:7669–7682. <https://doi.org/10.1007/s13197-015-1905-1>
- Ninago MD, Lopez OV, Lencina MMS, Garcia MA, Andreucetti NA, Ciolino AE, Villar MA (2015) Enhancement of thermoplastic starch final properties by blending with poly(epsilon-caprolactone). *Carbohydr Polym* 134:205–212. <https://doi.org/10.1016/j.carbpol.2015.08.007>
- Nisa IU, Ashwar BA, Shah A, Gani A, Gani A, Masoodi FA (2015) Development of potato starch based active packaging films loaded with antioxidants and its effect on shelf life of beef. *J Food Sci Technol Mysore* 52:7245–7253. <https://doi.org/10.1007/s13197-015-1859-3>
- Ortega-Toro R, Jimenez A, Talens P, Chiralt A (2014) Effect of the incorporation of surfactants on the physical properties of corn starch films. *Food Hydrocoll* 38:66–75. <https://doi.org/10.1016/j.foodhyd.2013.11.011>
- Ortega-Toro R, Morey I, Talens P, Chiralt A (2015) Active bilayer films of thermoplastic starch and polycaprolactone obtained by compression molding. *Carbohydr Polym* 127:282–290. <https://doi.org/10.1016/j.carbpol.2015.03.080>
- Peressini D, Bravin B, Lapasin R, Rizzotti C, Sensidoni A (2003) Starch-methylcellulose based edible films: rheological properties of film-forming dispersions. *J Food Eng* 59:25–32. [https://doi.org/10.1016/S0260-8774\(02\)00426-0](https://doi.org/10.1016/S0260-8774(02)00426-0)
- Sanyang ML, Sapuan SM, Jawaid M, Ishak MR, Sahari J (2016) Effect of plasticizer type and concentration on physical properties of biodegradable films based on sugar palm (*arenga pinnata*) starch for food packaging. *J Food Sci Technol Mysore* 53:326–336. <https://doi.org/10.1007/s13197-015-2009-7>
- Shankar S, Rhim JW (2016) Preparation of nanocellulose from microcrystalline cellulose: the effect on the performance and properties of agar-based composite films. *Carbohydr Polym* 135:18–26. <https://doi.org/10.1016/j.carbpol.2015.08.082>
- Singh N, Belton PS, Georget DMR (2009) The effects of iodine on kidney bean starch: films and pasting properties. *Int J Biol Macromol* 45:116–119. <https://doi.org/10.1016/j.jbiomac.2009.04.006>
- Sousa GM, Yamashita F, Soares MS (2016) Application of biodegradable films made from rice flour, poly(butylene adipate-co-terephthalate), glycerol and potassium sorbate in the preservation of fresh food pastas. *LWT Food Sci Technol* 65:39–45. <https://doi.org/10.1016/j.lwt.2015.07.054>
- Sun H, Shao X, Ma Z (2016) Effect of incorporation nanocrystalline corn straw cellulose and polyethylene glycol on properties of biodegradable films. *J Food Sci* 81:E2529–E2537. <https://doi.org/10.1111/1750-3841.13427>
- Thakhiw W, Devahastin S, Soponronnarit S (2014) Combined effects of drying methods, extract concentration, and film thickness on efficacy of antimicrobial chitosan films. *J Food Sci* 79:E1150–E1158. <https://doi.org/10.1111/1750-3841.12488>
- Tharanathan RN (2003) Biodegradable films and composite coatings: past, present and future. *Trends Food Sci Technol* 14:71–78. [https://doi.org/10.1016/S0924-2244\(02\)00280-7](https://doi.org/10.1016/S0924-2244(02)00280-7)
- Villarruel S, Giannuzzi L, River S, Pinotti A (2015) Changes induced by UV radiation in the presence of sodium benzoate in films formulated with polyvinyl alcohol and carboxymethyl cellulose. *Mater Sci Eng C Mater Biol Appl* 56:545–554. <https://doi.org/10.1016/j.msec.2015.07.003>
- Wang Z, Zhang N, Wang HY, Sui SY, Sun XX, Ma ZS (2014a) The effects of ultrasonic/microwave assisted treatment on the properties of soy protein isolate/titanium dioxide films. *LWT Food Sci Technol* 57:548–555. <https://doi.org/10.1016/j.lwt.2014.01.036>
- Wang Z, Zhou J, Wang XX, Zhang N, Sun XX, Ma ZS (2014b) The effects of ultrasonic/microwave assisted treatment on the water vapor barrier properties of soybean protein isolate-based oleic acid/stearic acid blend edible films. *Food Hydrocoll* 35:51–58. <https://doi.org/10.1016/j.foodhyd.2013.07.006>
- Wu MY, Wu YQ, Liu Z, Liu HQ (2012) Optically transparent poly(methyl methacrylate) composite films reinforced with electrospun polyacrylonitrile nanofibers. *J Compos Mater* 46:2731–2738. <https://doi.org/10.1177/0021998311431995>
- Wu WT, Dong Z, He JS, Yu J, Zhang J (2016) Transparent cellulose/laponite nanocomposite films. *J Mater Sci* 51:4125–4133. <https://doi.org/10.1007/s10853-016-9735-8>
- Zhong Y, Li YF (2014) Effects of glycerol and storage relative humidity on the properties of kudzu starch-based edible films. *Starch-Starke* 66:524–532. <https://doi.org/10.1002/star.201300202>
- Zhong T, Huang R, Sui SY, Lian ZX, Sun XX, Wan AJ, Li HL (2015) Effects of ultrasound treatment on lipid self-association and properties of methylcellulose/stearic acid blending films. *Carbohydr Polym* 131:415–423. <https://doi.org/10.1016/j.carbpol.2015.06.026>