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The plasticizing mechanism and effect of calcium chloride on starch/poly(vinyl alcohol) films

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ABSTRACT

Starch/poly(vinyl alcohol) (PVA) films were prepared with calcium chloride ($CaCl_2$) as the plasticizer. The micro morphology of pure starch/PVA film and $CaCl_2$ plasticized starch/PVA film was observed by scanning electron microscope. The interaction between $CaCl_2$ and starch/PVA molecules was investigated by Fourier transform infrared spectroscopy. The influence of $CaCl_2$ on the crystalline, thermal and mechanical properties of starch/PVA films was studied by X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis, and tensile testing, respectively. The results indicated that $CaCl_2$ could interact with starch and PVA molecules and then effectively destroy the crystals of starch and PVA. Starch/PVA films plasticized with $CaCl_2$ became soft and ductile, with lower tensile strength and higher elongation at break compared with pure starch/PVA film. The water content of starch/PVA film would increase with the addition of $CaCl_2$. This is an important cause of the plasticization of $CaCl_2$ on starch/PVA film.

1. Introduction

Polymeric materials made from petroleum have been widely used throughout the world. However, the increasing use of polymeric materials has led to the problem of the disposal of post consumer plastic items when they become waste. Therefore the development of bio-based materials and synthetic biodegradable materials has attracted much attention. Starch is one of the most promising candidates for the future, primarily because of an attractive combination of availability, price and performance. However, the use of starch in the preparation of starch and starch-based biomaterials, such as packaging films and agricultural plastic films, is limited by its multi-hydroxyl and regular crystal structure (Park, Chough, Yun, & Yoon, 2005; Yao et al., 2011). Pure starch films are readily broken into fragments when they are dried at ambient temperature. Starch is normally modified by several methods such as blending with other synthetic or natural polymers (Huneault & Li, 2007; Landreau, Tighzert, Bliard, Berzin, & Lacoste, 2009; Sarazin, Li, Orts, & Favis, 2008), being reinforced with fillers like clay (Chiou, Yee, Glenn, & Orts, 2005; Wilhelm, Sierakowski, Souza, & Wypych, 2003), cellulose crystallites (Averous & Boquillon, 2004; Lu, Weng, & Cao, 2006), and also by crosslinking (Sreedhar, Sairam, Chattopadhyay, Syamala Rathnam, & Mohan Rao, 2005; Sreedhar, Chattopadhyay, Karunakar, & Sastry, 2006). Blending with other polymers is an effective way to improve the properties of starch film. Poly(vinyl alcohol) (PVA) is one of the synthetic biodegradable polymers to be produced on a large scale commercially and has been utilized in various industrial applications, such as fibers, films, hydrogels, and glues (Yan & Tang, 2003, chap. 4). In addition, PVA is one of the few polymers that can be produced via a non-petroleum route (Chen, Li, & Wang, 2007). Blending of PVA and starch is favorable because both of them are polar substances which have many hydroxyl groups in their chemical structure. These highly polar hydroxyl groups tend to form intermolecular and intramolecular hydrogen bonds. The formation of hydrogen bonds between hydroxyl groups of starch and PVA tends to promote the localized stability and subsequently improve the miscibility of starch and PVA (Sin, Rahman, Rahmat, & Samad, 2010). Moreover, both starch and PVA are biodegradable and readily consumed by microorganisms in the natural environment. Starch/PVA blend plastics have been one of the most popular biodegradable plastics widely used in packaging and agricultural applications (Jayasekara, Harding, Bowater, Christie, & Lonergan, 2004; Liu, Feng, & Yi, 1999; Ray et al., 2009; Shogren, Lawton, Tiefenbacher, & Chen, 1998; Tudorachi, Cascaval, Rusu, & Pruteanu, 2000; Zhai, Yoshii, Kume, & Hashim, 2002; Zhao et al., 2006; Zhu, 2003).

Starch and starch-based films are commonly plasticized to overcome the brittleness and to avoid the cracking of films during subsequent handling and storage. Many researchers have studied the effects of various plasticizers on the starch and starch-based

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films (Dai, Chang, Geng, Yu, & Ma, 2010; Hulleman, Janssen, & Feil, 1998; Ma, Yu, & He, 2006; Ma, Yu, & Wan, 2006; Park et al., 2005; Talja, Helen, Ross, & Jouppila, 2007; Zhang & Han, 2006). The most commonly used plasticizers for starch and PVA were polyols such as glycerol, sorbitol, and poly(ethylene glycol) and monosaccharides such as mannose, glucose and fructose (Zhang & Han, 2006). The basic principles of the plasticizing of these plasticizers are those: (1) the plasticizers contain many hydroxyl groups and these hydroxyl groups can form intermolecular hydrogen bonds with the hydroxyl groups of starch and thus reduce the intermolecular hydrogen bonds and entanglements between polymer chains. (2) the plasticizers can increase the water content of starch and PVA and water has the plasticizing effect for starch and PVA. Several studies have been done using monosaccharides as the plasticizer for starch. But the plasticizing efficiency of these plasticizers is limited and the compatibility between these plasticizers and starch is poor (Zhang & Han, 2006).

The plasticizing efficiency and compatibility are the two main criterions for selecting the plasticizer. Usually the plasticizing efficiency of the plasticizers could be enhanced with the content. But the phase separation between the plasticizer and polymer would occur at high plasticizer content. Previous work has proved that some metal salts have a high plasticizing efficiency for PVA and the compatibility between these metal salts and PVA was very good (Bhajantri, Ravindrachary, Harisha, & Crasta, 2006; Kubo et al., 2009). Our research group has studied the plasticizing effect of $MgCl_2$ on PVA and has successfully realized the melt processing of PVA with $MgCl_2$ as the plasticizer (Jiang, Jiang, Zhang, Dai, & Zhang, 2012; Jiang, Zhang, Ye, Zhang, & Dai, 2012). Based on the common ground between the molecule structure of starch and PVA, we conclude that these metal salts would have a high plasticizing efficiency for starch films.

Many researchers have doped metal halides into starch to prepare the solid ion-conducting materials (Finkenstadt & Willett, 2004; Ma, Yu, & He, 2006; Ma, Yu, & Wan, 2006). It was observed that the metal salts, such as NaCl, LiCl, and KCl, could interact with starch molecules and restrain the recrystallization of starch. In this paper, calcium chloride ($CaCl_2$) was used to modify the properties of starch/PVA films. The plasticizing mechanism of $CaCl_2$ was discussed and the crystalline, thermal and mechanical properties of $CaCl_2$ plasticized starch/PVA films were studied.

2. Materials and methods

2.1. Materials

Soluble starch (potato starch, with the water content of 12%) was provided by Kelong chemical Co. (Chengdu, China). PVA (DP = 1750, degree of hydrolysis 99%) was provided by Sichuan Vinylon Factory, SINOPEC (China). The commercial PVA products were used after washing several times with distilled water until a pH of 7 was attained, and were dried at 60 °C to a constant weight. $CaCl_2$ was purchased from Kelong chemical Co. (Chengdu, China).

2.2. Preparation of the films

Starch/PVA films were prepared by the casting method. Firstly, 2.5 g starch, 2.5 g PVA and the calculated amount of $CaCl_2$ were dissolved in 95.0 g distilled water by heating in an oil bath at 95 °C for 2 h, and the about 5 wt% starch/PVA aqueous solutions were prepared, which was called the film-forming solution. The film-forming solutions were casted onto the Petri dishes and dried at 60 °C for 12 h to completely eliminate water. In this way starch/PVA films with the thickness of about 0.2 mm were obtained. These films were stored at relative humidity of 54% for one week before testing. The 54% relative humidity was obtained in a sealed chamber containing saturated $Mg(NO_3)_2$ solution at 25 °C. Starch/PVA film with 0 wt%, 5 wt%, 10 wt%, 15 wt% and 20 wt% (weight base of the total of starch and PVA) were prepared and named SP, SPC5, SPC10, SPC15 and SPC20, respectively.

2.3. Fourier transform infrared (FT-IR) spectroscopy

The infrared spectra were measured with a Fourier transform infrared spectrophotometer (Nicolet 560). The film-forming solutions were casted onto the Petri dishes and dried at 60 °C to completely eliminate water. The measurements were carried out with a resolution of $4\,cm^{-1}$ and 32 scans.

2.4. Water content

The water content of the films at the relative humidity of 54% was determined by thermogravimetric method. The films were first stored at relative humidity of 54% for one week and then dried at 100 °C for 12 h. The water content (WC) was calculated as the following equation:

$$WC = \frac{W_e - W_d}{W_d}$$

where W_e is the weight of the films after storing at relative humidity of 54% for one week and W_d is the weight of the films after dried at 100 °C.

2.5. X-ray diffraction (XRD) measurements

X-ray diffraction patterns were recorded in the reflection mode in the angular range of 3–50° (2θ) at ambient temperature by an X'Pert Pro MPD diffractometer. The radiation from the anode, operating at 50 kV and 35 mA, monochromized with a nickel foil. The measurements were performed at a scanning speed of $2\theta = 0.06^\circ\,s^{-1}$.

2.6. Scanning electron microscopy (SEM)

The cross section of the films was observed on an Inspect SEM instrument (JSM-5900LV, Japan). The samples were first freeze-fractured by liquid nitrogen. The fracture surfaces were vacuum coated with gold and examined with the acceleration voltage of 20 kV.

2.7. Differential scanning calorimetry (DSC)

The glass transition temperatures were measured by a differential scanning calorimeter (NETZSCH DSC 204). Slices of the modified PVA films with total weight of 5–7 mg were weighted and sealed in aluminum pans. The pans were heated from −80 °C to 60 °C at a rate of 10 °C/min under a flow of nitrogen.

2.8. Thermogravimetric analysis (TGA)

TGA was performed by TA 2950 TGA thermal analysis instrument (DuPont). The samples were about 5–10 mg in a sealed aluminum pan. The scope of the testing temperature was from room temperature to 600 °C at a heating rate of 10 °C/min.

2.9. Tensile testing

The tensile strength, Young's modulus, and elongation at break of PVA films were tested by extension measurements at room temperature using a tensile tester (Instron 5567). The crosshead speed was 20 mm/min. The initial gauge length of the specimen was 20 mm. The width of each tensile sample was 4 mm. Thickness of the film was measured with a micrometer in triplicate. Samples were equilibrated in vacuum desiccators over the saturated solution of $Mg(NO_3)_2$ giving RH of 54% for 72 h before mechanical testing. The data were the average of 5–7 specimens.

2.10. Dynamic mechanical analysis (DMA)

The dynamic mechanical measurements were carried out with DMA Q800 (TA Instruments, DE, USA). In all tests the samples with approximate dimension of 15.0 mm × 4.0 mm × 0.2 mm were cut from starch/PVA film. The oscillatory frequency of the dynamic test was 1 Hz, and the temperature was raised from −60 to 100 °C at a constant rate of 3 °C/min.

3. Results and discussion

3.1. The plasticizing mechanism of $CaCl_2$ on starch/PVA

The highly polar hydroxyl groups in both starch and PVA molecules could easily form the intermolecular and intramolecular hydrogen bonds. The formation of hydrogen bonds between the hydroxyl groups of starch and PVA would promote the localized stability and subsequently improve the miscibility of starch and PVA. But the hydrogen bonding also controls the thermal properties of starch and PVA and makes the thermal processing of starch and PVA difficult. The plasticization of starch and PVA needs to reduce the intensity of the self intramolecular and intermolecular hydrogen bonding in starch and PVA molecules. The intensity of the hydrogen bonds can be identified by the analysis of FT-IR spectra of starch/PVA films (Sin et al., 2010). The indication and diagnosis of the infrared absorption on the formation of hydrogen bonds can be found in the FT-IR spectrum at the range of 3300–3400 cm^{-1}.The vibration of absorption within this range is affected by the number and intensity of hydrogen bonds. The formation of hydrogen bonds weakens the O—H bond which will cause the band elongation and lead to a lower O—H stretching frequencies. This phenomenon is known as “red shift” by He et al. This shift provides obvious and meaningful information about the formation of hydrogen bond within species (He, Zhu, & Inoue, 2004). One of the basic principles of the common used plasticizers such as glycerol is that the plasticizer can form interaction with starch and PVA molecules and replace the self intramolecular and intermolecular hydrogen bonding. Ma et al. studied the interaction between starch and plasticizers in the thermoplastic starch, which could be identified by the FT-IR spectra and thought that the lower the peak frequency the stronger the interaction was (Ma & Yu, 2004).

Fig. 1 shows the FT-IR spectra of pure starch/PVA and starch/PVA films plasticized with varying content of $CaCl_2$. Both the deformation vibration of $–CH_2$ in $–CH_2OH$ of PVA molecule at 1422 cm^{-1} and the characteristic of the anhydroglucose ring O—C stretch in starch at 1029 cm^{-1} were found in the FT-IR spectra of starch/PVA films (Jiang, Xu, Tang, Zhang, & Dai, 2010; Ma, Yu, & He, 2006; Ma, Yu, & Wan, 2006). From Fig. 1 it can be noted that starch/PVA films exhibited a decrease in frequencies after the addition of $CaCl_2$. The absorption frequency of hydroxyl group shifted from 3353 cm^{-1} of pure starch/PVA to 3338, 3343, 3328, 3349 cm^{-1} with the $CaCl_2$ content increased from 5 wt% to 20 wt%, respectively. This indicated that $CaCl_2$ could form strong interaction with starch and PVA molecules and this interaction was enhanced with the content of $CaCl_2$. The absorption frequency of hydroxyl group of SPC20 shifted to 3349 cm^{-1}, higher than that of SPC5 (3338 cm^{-1}). This is because that with the interaction between $CaCl_2$ and starch/PVA molecules the hydrogen bonding within starch and PVA molecules was weakened (Viota, Lopez-Viota, Saake, Stana-Kleinschek, & Delgado, 2010). The weakening of the hydrogen bonding would lead the frequency shifted to a high value. The peak at 1029 cm^{-1} is the characteristic of the anhydroglucose ring O—C stretch. The shift of this peak to a lower wavenumber indicated that $CaCl_2$ could form strong interaction with O of anhydroglucose ring O—C in starch molecules. This is in agreement with the selective adsorption of calcium ion by starch molecule previously reported by J. Hollo et al. (Hollo, Huszar, Szejtui, & Petho, 1962). Another characteristic peak occurred at 1648 cm^{-1} was the feature of tightly bound water present in starch and PVA.

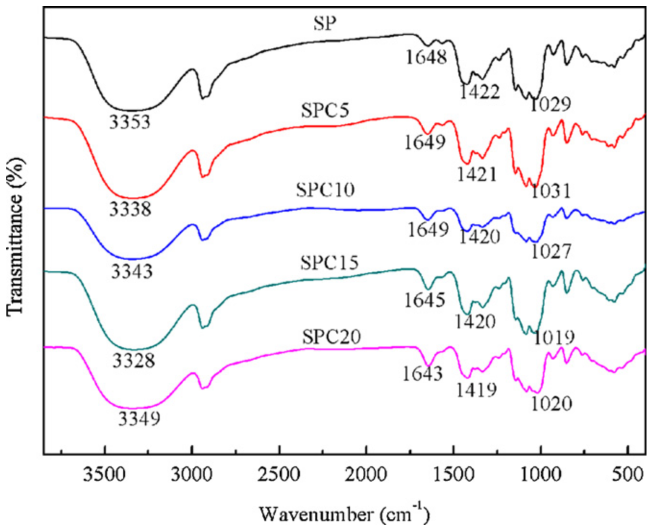

Fig. 1. The FT-IR spectra of SP, SPC5, SPC10, SPC15 and SPC20.

However, previous studies show that the strong interaction between metal ions and the hydroxyl group does not guarantee the plasticization effect of metal salts on polysaccharose such as chitosan. The metal salts with the quantivalent ion may also act as the cross-linker. To ensure the plasticizing effect of metal salt on starch and PVA, the metal salt should be hydrate salt or can increase the water content of starch/PVA film (Hirase, Higashiyama, Mori, Takahara, & Yamane, 2010). Another principle of the plasticization of starch and PVA is that the plasticizers are hydrophilic and can attract water around the starch and PVA molecules. Water is an effective plasticizer for both starch and PVA. $CaCl_2$ is highly hydrophilic and can be used as the desiccating agent. The water content of starch/PVA film plasticized with varying content of $CaCl_2$ at relative humidity of 54% was determined and recorded in Table 1. From Table 1 it can be seen that the water content of starch/PVA films increased rapidly with the increment of $CaCl_2$ content.

From the above studies it can be proved that $CaCl_2$ can strongly interact with starch and PVA molecules and increase the water content of starch/PVA film. This is the two important causes of the plasticization of $CaCl_2$ on starch/PVA film. This is in agreement with the principles of the common used plasticizers for starch and PVA.

3.2. The effect of $CaCl_2$ on the crystalline properties of starch/PVA

The X-ray diffraction patterns of pure starch, PVA and starch/PVA films plasticized with varying content of $CaCl_2$ are displayed in Fig. 2. From Fig. 2a it can be seen that pure PVA shows the diffraction peak at $2\theta = 20^\circ$ ($d = 0.45$ nm) and starch

Table 1
Water content of SP, SPC5, SPC10, SPC15 and SPC20 at the relative humidity of 54%.

Sample	SP	SPC5	SPC10	SPC15	SPC20
WC (%)	13.56	15.42	19.14	22.68	29.61

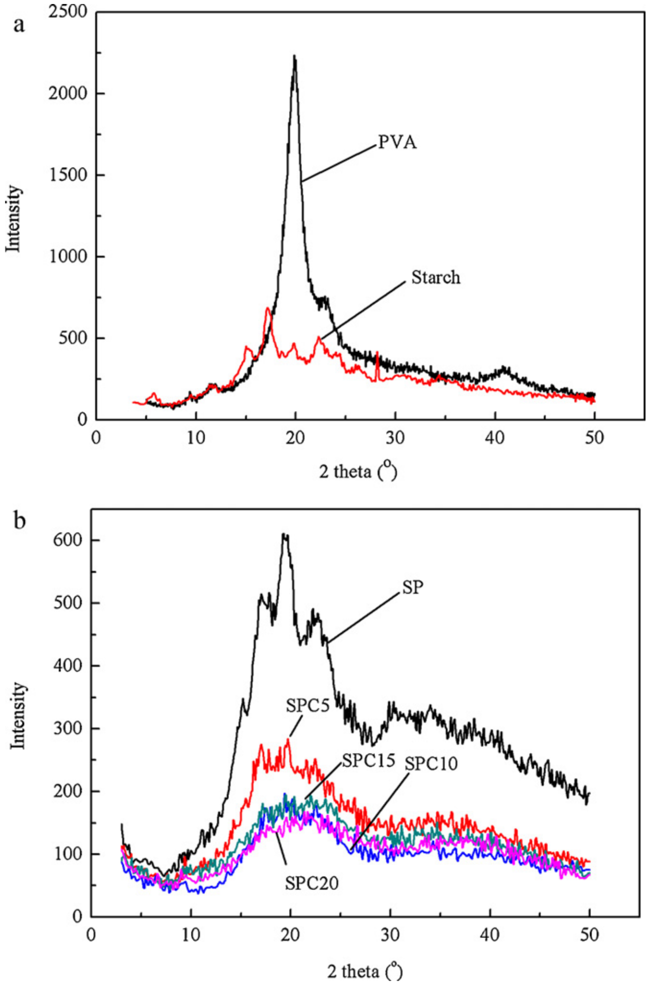

Fig. 2. XRD curves of pure starch and PVA (a) and starch/PVA films with varying content of $CaCl_2$ (b).

shows the diffraction peaks at $2\theta = 17°$ ($d = 0.52$ nm) and $2\theta = 22°$ ($d = 0.40$ nm) of B-type crystal of starch. The diffraction peaks at $2\theta = 17°$ ($d = 0.52$ nm) and $2\theta = 22°$ ($d = 0.40$ nm) of B-type crystal of starch and $2\theta = 20°$ ($d = 0.46$ nm) of PVA crystal were also obviously shown in the X-ray diffractogram of pure starch/PVA film as shown in Fig. 2b (Hulleman et al., 1998). This shows that the blend of starch and PVA cannot effectively break the crystals of starch and PVA. With the addition of $CaCl_2$, the diffraction peaks of starch/PVA film decreased rapidly in intensity and some crystal peaks almost disappeared with the increasing of $CaCl_2$ content. This indicated that the addition of $CaCl_2$ could effectively destroy the crystals of starch and PVA. This is because that $CaCl_2$ could form strong interaction with starch and PVA molecules and this interaction would interrupt the intermolecular hydrogen bonding in starch and PVA crystals. With the crystals of both starch and PVA destroyed, starch and PVA molecules could form more interaction with each other. This would contribute to the improvement of the compatibility of starch and PVA. The previous work has proved that the area under the diffraction peak or its intensity could be taken as a measurement of the degree of crystallinity. The decrease of the intensity of the diffraction peak indicated that the addition of $CaCl_2$ could effectively decrease the degree of crystallinity of starch/PVA films. It could also be noticed that the Bragg peaks of $CaCl_2$ did not show even in the diffractogram of SPC20. This also suggests that $CaCl_2$ is completely dissolved in starch/PVA film and no $CaCl_2$ crystals or congregates exist. The water in starch/PVA film can also destroy the crystal of starch and PVA and decrease its crystallinity.

3.3. *The effect of $CaCl_2$ on the morphology of starch/PVA*

Starch and PVA molecules could associate with each other by intermolecular and intramolecular hydrogen bonding. It can be seen with naked eyes that starch/PVA films would become more homogeneous and ductile with the addition of $CaCl_2$. Fig. 3 shows the SEM figures of the cross section of pure starch/PVA film and starch/PVA film plasticized with 20 wt% $CaCl_2$. It was observed from Fig. 3a that the granular structure of starch was not fully destroyed even after the gelatinization was done. PVA formed a continuous phase and starch was dispersed in PVA matrix. The exposures of starch granules blended with PVA were visible in pure starch/PVA film under scanning electron microscope, indicating that starch and PVA was partially compatible. Starch and PVA formed a homogeneous phase with the addition of 20 wt% $CaCl_2$ and no starch granules were observed. This indicated that $CaCl_2$ could effectively improve the compatibility between starch and PVA. The improvement of the compatibility of starch and PVA could be attributed to that $CaCl_2$ could effectively destroy the crystals of starch and PVA. With the crystals being destroyed, the entanglements and interaction between starch and PVA molecules would be enhanced. The improvement of the compatibility between starch and PVA would greatly enhance the mechanical properties of starch/PVA films. It could also be noticed that no $CaCl_2$ crystals or congregates could be observed on the cross section of 20 wt% $CaCl_2$ plasticized starch/PVA. This means that $CaCl_2$ could be completely dissolved in starch/PVA matrix.

3.4. *The effect of $CaCl_2$ on the T_g of starch/PVA*

The T_g value of a polymer can be modified by blending with a small amount of additive. This phenomenon is called plasticization when it ends up with a decrease of T_g. Most of the plasticizers

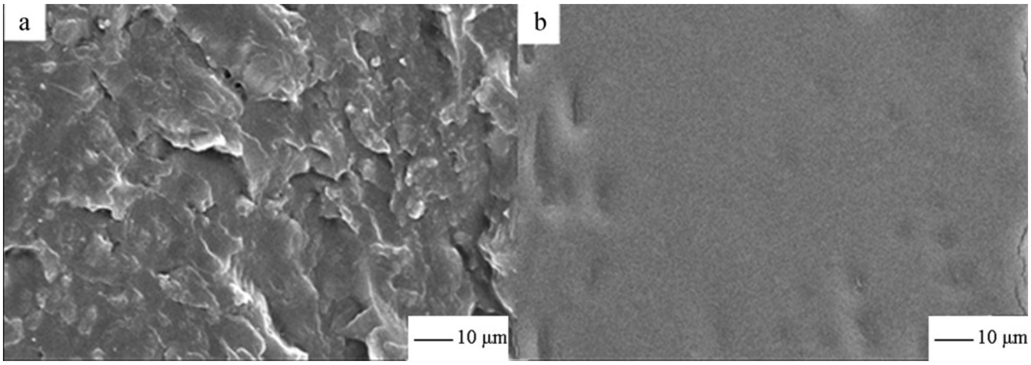

Fig. 3. SEM micrographs of SP (a) and SPC20 (b).

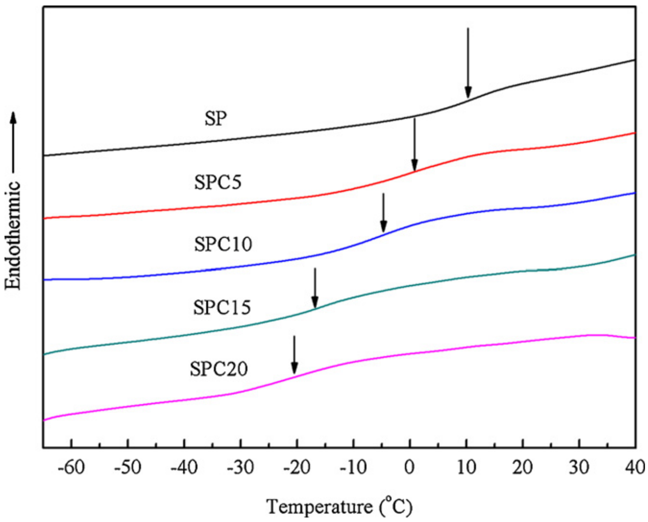

Fig. 4. DSC thermograms of SP, SPC5, SPC10, SPC15 and SPC20 from −65 to 40 °C.

used for starch and PVA could decrease T_g of starch and PVA. The research of Talja et al. has shown that various polyols such as glycerol, xylitol and sorbitol can decrease T_g of potato starch-based films (Talja et al., 2007). Our previous research has proved that $MgCl_2 \cdot 6H_2O$ can effectively decrease T_g of PVA (Jiang, Jiang, et al., 2012; Jiang, Zhang, et al., 2012). The influence of $CaCl_2$ on T_g of starch/PVA films was determined by DSC measurements. The measurements were carried out from −70 to 50 °C at a heating rate of 10 °C/min. The obtained DSC thermograms are shown in Fig. 4. In the present study only single glass transition was observed on each DSC thermogram and T_g decreased monotonously with the content of $CaCl_2$. Only single glass transition also indicates that starch and PVA are compatible. But the distinct reunion of starch granules in pure starch/PVA film could be observed with naked eyes. This means that starch and PVA are just partly compatible. With the addition of $CaCl_2$ the T_g value decreased from 11.6 °C of SP to 0.3 °C of SPC5, −5.1 °C of SPC10, −15.8 °C of SPC15 and −20.3 °C of SPC20. The decrease of T_g indicated that the chain mobility of starch and PVA increased. This is mainly because that $CaCl_2$ could interact with starch and PVA molecules and the interchain molecular hydrogen bonding within starch and PVA molecules is interrupted. This is similar with the situation of monosaccharides and polyols plasticized starch based film (Zhang & Han, 2006).

3.5. The effect of $CaCl_2$ on the thermal stability of starch/PVA

The influence of $CaCl_2$ on the thermal stability of starch/PVA films was evaluated by thermogravimetric analysis. To eliminate the influence of water, the samples for TGA measurement were dried at 100 °C to completely eliminate water. Fig. 5 shows the obtained TGA mass loss curves and DTG curves for pure starch/PVA film and $CaCl_2$ plasticized starch/PVA films. It was shown that the addition of $CaCl_2$ would largely influence the thermal degradation behavior of starch/PVA film. Pure starch/PVA film started to decompose at 276 °C. With the addition of $CaCl_2$, starch/PVA film would start the thermal decomposition at a lower temperature. It could be seen from Fig. 5 that the peak position also shifted to a lower temperature, indicating that the thermal degradation process of starch/PVA happened at a lower temperature. The residue at 600 °C increased sharply with the increasing of the content of $CaCl_2$. This is because that $CaCl_2$ is very stable even at 600 °C and the increased content of $CaCl_2$ would increase the residue at 600 °C. The peaks at around 430–440 °C in the DTG curves were the second thermal decomposition peak of PVA.

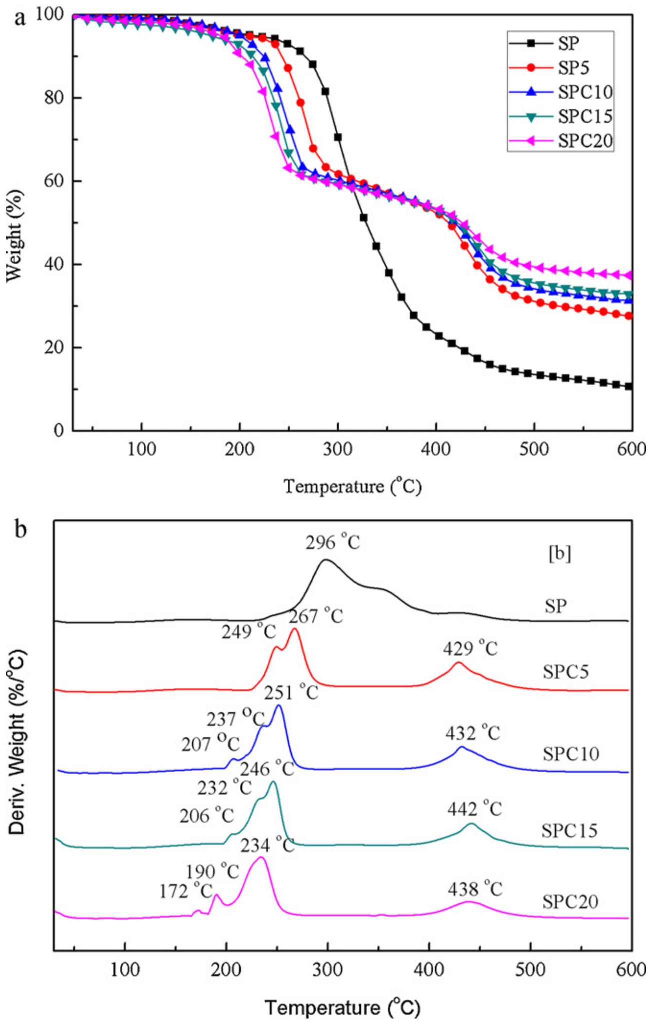

Fig. 5. TGA (a) and DTG (b) curves of SP, SPC5, SPC10, SPC15 and SPC20.

Previous studies have proved that the decomposition of PVA follows a two-step mechanism. The first decomposition step mainly involves the dehydration of the hydroxyl groups. This is followed by the formation of volatile organic compounds which subsequently produced conjugated unsaturated polyene structures. Starch has the same trend of degradation because starch also consists of hydroxyl groups. The thermal stability of a polymeric material depends on the inherent characteristics of the samples as well as on the interaction between the different macromolecules. Pure PVA started the decomposition at 229 °C. When starch/PVA films were prepared, the intercomponent hydrogen bonds between starch and PVA would increase the thermal stability. But with the addition of $CaCl_2$, the crystals of starch and PVA were destroyed and the degree of crystallinity of starch/PVA films decreased. With the increment of the amorphous fraction, the decomposition would be more easily to happen. These two effects would affect the thermal stability of starch/PVA film. The T_i (the initial decomposition temperature) of starch/PVA film decreased with the increasing content of $CaCl_2$. This indicated that with the addition of $CaCl_2$ the thermal stability of starch/PVA film decreased.

3.6. The effect of $CaCl_2$ on the mechanical properties of starch/PVA

Pure starch/PVA film was wavy, rigid and brittle. The poor mechanical property of starch or starch-based film has restricted the development of starch and starch-based film. During

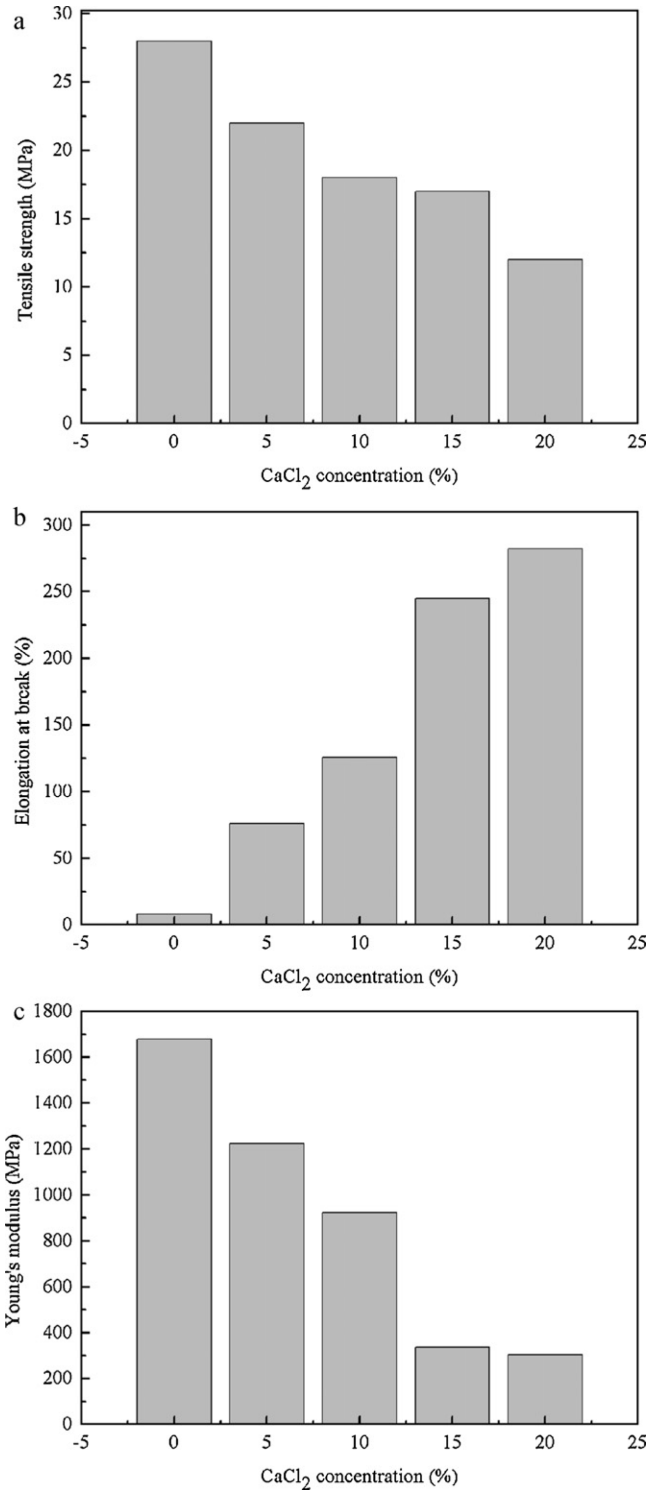

Fig. 6. Effect of CaCl$_2$ concentration on the tensile strength, elongation at break and Young's modulus of starch/PVA films (a) for tensile strength, (b) for elongation at break, and (c) for Young's modulus.

experiment pure starch/PVA film was fragile and difficult to handle. After adding CaCl$_2$ starch/PVA films would become flexible and easy to handle. The influence of CaCl$_2$ on the mechanical properties of starch/PVA films was evaluated by tensile testing. Fig. 6 shows the measured values of tensile strength, elongation at break and Young's modulus of starch/PVA films plasticized with varying content of CaCl$_2$. As shown in Fig. 6, with the increasing of the content of CaCl$_2$, the tensile strength of starch/PVA film decreased slightly. The tensile strength decreased from 28 MPa of pure starch/PVA film to 22, 18, 17, 12 MPa with the content of CaCl$_2$ increased from 5 wt% to 20 wt%, respectively. Meanwhile, the elongation at break of starch/PVA films increased rapidly. The elongation at break of pure starch/PVA film was 8%, suggesting that pure starch/PVA film was rigid and brittle. With the addition of just 5% CaCl$_2$, the elongation at break of starch/PVA film increased to 76%. The elongation at break of starch/PVA film could reach to 282% with 20 wt% CaCl$_2$. Young's modulus of starch/PVA films also decreased with the addition of CaCl$_2$. The decrease of tensile strength and Young's modulus and the increase of the elongation at break prove that CaCl$_2$ has the plasticizing effect for starch/PVA film. Most of the plasticizers can decrease the tensile strength and increase the elongation at break of starch/PVA film. The research of Park et al. shows that citric acid has a high plasticizing efficiency for starch/PVA film than glycerol. But the elongation of starch/PVA films adding 50 wt% citric acid still could not exceed 150% (Park et al., 2005). By comparison it can be concluded that CaCl$_2$ is of a higher plasticizing efficiency for starch/PVA films than the commonly used plasticizers.

3.7. *The effect of CaCl$_2$ on the dynamic mechanical properties of starch/PVA*

DMA has been widely used in the determination of the material properties. DMA can supply information on the interaction between different components at molecular level as the dynamic mechanical properties of polymers can sensitively represent their molecular motion, which has a close relationship with the chain structures of polymer (Wang, Li, Wang, Yang, & Ozkan, 2011). Fig. 7 shows the plots of storage modulus (G′) and tan δ versus temperature for pure starch/PVA film and CaCl$_2$ plasticized starch/PVA films. It can be seen from Fig. 7 that G′ of starch/PVA film decreased with the addition of CaCl$_2$. This is because that CaCl$_2$ could form strong interaction with starch and PVA molecules and the crystals of starch and PVA are destroyed as shown by the FT-IR and XRD studies. G′ gradually decreased with the increasing content of CaCl$_2$. This meant that the plasticizing effect was enhanced with the content of CaCl$_2$. G′ is a measurement of the stiffness (rigidity) of the material. The decreasing of G′ meant that starch/PVA film became softer.

Tan δ is a damping term defined as the ration of energy dissipated as heat to the maximum energy stored in the materials. It is an index of the material viscoelasticity. It can be seen from Fig. 7b that the tan δ values of starch/PVA films increased with the increasing content of CaCl$_2$. This indicated that with the increasing content of CaCl$_2$, the viscoelasticity of starch/PVA films increased. The size of the tan δ peak is believed to relate to the volume fraction of the material undergoing the transition. For CaCl$_2$ plasticized starch/PVA films, the peak size of tan δ increased larger as the CaCl$_2$ content increased from 5% to 20%. This is because that the degree of crystallinity of starch/PVA film decreased with the addition of CaCl$_2$ and the amorphous fraction of starch/PVA increased. This is in agreement with the change of the dynamic mechanical properties of polymer materials with the addition of plasticizer. In DMA studies the peak temperature of the δ curve is also determined as the T_g of the polymer material. It is interesting to see from Fig. 7b that the T_g decreased slightly with the content of CaCl$_2$. This is different from the results of DSC studies. This may be ascribed to the difference between the two analytical methods. As noted previously, the discrepancy observed in the values of T_g by DSC and DMA is due to principles involved in the methods of measurement and different constraint on sample and heating rates (Miura, Kimura, Suzuki, Miyashita, & Nishio, 1999). In DMA measurement the structural reorganization during dynamic process would happen (Gohil, 2011).

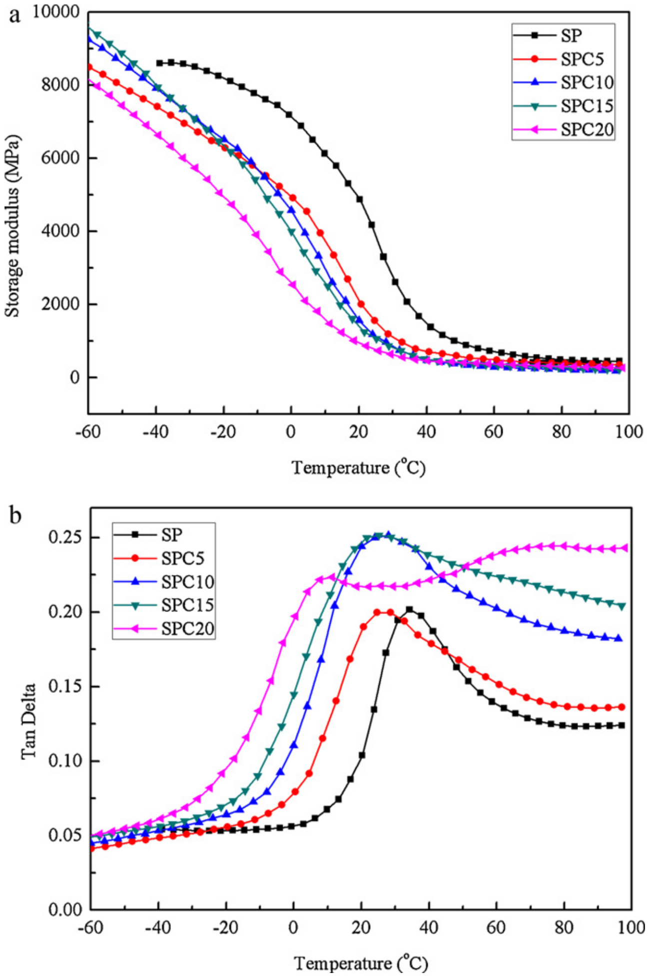

Fig. 7. Plots of storage modulus (a) and tan δ (b) versus temperature of SP, SPC5, SPC10, SPC15 and SPC20.

4. Conclusions

The results in this paper have effectively demonstrated that $CaCl_2$ can be used as the plasticizer for starch/PVA film. The plasticizing mechanism of $CaCl_2$ on starch/PVA is in agreement with the mechanism of the common used plasticizers for starch and PVA. $CaCl_2$ could form strong interaction with starch and PVA molecules and the addition of $CaCl_2$ can increase the water content of starch/PVA films. With the addition of $CaCl_2$ the compatibility between starch and PVA would be improved and starch/PVA film appeared a more continuous phase. The glass transition temperature and the thermal stability of starch/PVA films decreased with the addition of $CaCl_2$. The addition of $CaCl_2$ can remarkably improve the mechanical properties of starch/PVA film and overcome the brittleness of starch/PVA film. It can also be expected that $CaCl_2$ could act as the plasticizer for other polymers such as cellulose that contain a lot of hydroxyl groups.

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References

Averous, L., & Boquillon, N. (2004). Biocomposites based on plasticized starch: Thermal and mechanical behaviours. *Carbohydrate Polymers*, *56*, 111–122.

Bhajantri, R. F., Ravindrachary, V., Harisha, A., & Crasta, V. (2006). Microstructural studies on $BaCl_2$ doped poly(vinyl alcohol). *Polymer*, *47*, 3591–3598.

Chen, N., Li, L., & Wang, Q. (2007). New technology for thermal processing of poly(vinyl alcohol). *Plastics, Rubber and Composites*, *36*, 283–290.

Chiou, B. S., Yee, E., Glenn, G. M., & Orts, W. J. (2005). Rheology of starch–clay nanocomposites. *Carbohydrate Polymers*, *59*, 467–475.

Dai, H. G., Chang, P. R., Geng, F. Y., Yu, J. G., & Ma, X. F. (2010). Preparation and properties of starch-based film using N,N-bis(2-hydroxyethyl)formamide as a new plasticizer. *Carbohydrate Polymers*, *79*, 306–311.

Finkenstadt, V. L., & Willett, J. L. (2004). Electroactive materials composed of starch. *Journal of Polymers and the Environment*, *12*, 43–46.

Gohil, R. M. (2011). Synergistic blends of natural polymers, pectin and sodium alginate. *Journal of Applied Polymer Science*, *120*, 2324–2336.

He, Y., Zhu, B., & Inoue, Y. (2004). Hydrogen bonds in polymer blends. *Progress in Polymer Science*, *29*, 1021–1051.

Hirase, R., Higashiyama, Y., Mori, M., Takahara, Y., & Yamane, C. (2010). Hydrated salts as both solvent and plasticizer for chitosan. *Carbohydrate Polymers*, *80*, 993–996.

Hollo, J., Huszar, J., Szejtui, J., & Petho, M. (1962). Neuere Beiträge zur Chemie der Stärkefraktionen. XII. Untersuchung des Calcium- und Magnesium-Adsorptionsvermögens der Stärkekörner. *Stärke*, *14*, 343–347.

Hulleman, S. H. D., Janssen, F. H. P., & Feil, H. (1998). The role of water during plasticization of native starches. *Polymer*, *39*, 2043–2048.

Huneault, M. A., & Li, H. B. (2007). Morphology and properties of compatibilized polylactide/thermoplastic starch blends. *Polymer*, *48*, 270–280.

Jayasekara, R., Harding, I., Bowater, I., Christie, G. B. Y., & Lonergan, G. T. (2004). Preparation surface modification and characterisation of solution cast starch PVA blended films. *Polymer Testing*, *23*, 17–27.

Jiang, X. C., Jiang, T., Zhang, X. F., Dai, H., & Zhang, X. (2012). Melt processing of poly(vinyl alcohol) through adding magnesium chloride hexahydrate and ethylene glycol as a complex plasticizer. *Polymer Engineering and Science*, http://dx.doi.org/10.1002/pen.23166

Jiang, X. C., Xu, W. P., Tang, Y. D., Zhang, X., & Dai, H. (2010). Studies on properties of PVA film plasticized with mixture of urea/ethanolamine. *Acta Polymerica Sinica*, *9*, 1143–1147.

Jiang, X. C., Zhang, X. F., Ye, D. Z., Zhang, X., & Dai, H. (2012). Modification of poly(vinyl alcohol) films by the addition of magnesium chloride hexahydrate. *Polymer Engineering and Science*, *52*, 1565–1570.

Kubo, J. I., Rahman, N., Takahashi, N., Kawai, T., Matsuba, G., Nishida, K., et al. (2009). Improvement of poly(vinyl alcohol) properties by the addition of magnesium nitrate. *Journal of Applied Polymer Science*, *112*, 1647–1652.

Landreau, E., Tighzert, L., Bliard, C., Berzin, F., & Lacoste, C. (2009). Morphologies and properties of plasticized starch/polyamide compatibilized blends. *European Polymer Journal*, *45*, 2609–2618.

Liu, Z. Q., Feng, Y., & Yi, X. S. (1999). Thermoplastic starch/PVAl compounds: Preparation, processing and properties. *Journal of Applied Polymer Science*, *74*, 2667–2673.

Lu, Y. S., Weng, L. H., & Cao, X. D. (2006). Morphological, thermal and mechanical properties of ramie crystallites – reinforced plasticized starch biocomposites. *Carbohydrate Polymers*, *63*, 198–204.

Ma, X. F., & Yu, J. G. (2004). Formamide as the plasticizer for thermoplastic starch. *Journal of Applied Polymer Science*, *93*, 1769–1773.

Ma, X. F., Yu, J. G., & He, K. (2006). Thermoplastic starch plasticized by glycerol as solid polymer electrolytes. *Macromolecular Materials and Engineering*, *291*, 1407–1413.

Ma, X. F., Yu, J. G., & Wan, J. J. (2006). Urea and ethanolamine as a mixed plasticizer for thermoplastic starch. *Carbohydrate Polymers*, *64*, 267–273.

Miura, K., Kimura, N., Suzuki, H., Miyashita, Y., & Nishio, Y. (1999). Thermal and viscoelastic properties of alginate/poly(vinyl alcohol) blends cross-linked with calcium tetraborate. *Carbohydrate Polymers*, *39*, 139–144.

Park, H. R., Chough, S. H., Yun, Y. H., & Yoon, S. D. (2005). Properties of starch/PVA blend films containing citric acid as additive. *Journal of Polymers and the Environment*, *13*, 375–382.

Ray, D., Roy, P., Sengupta, S., Sengupta, S. P., Mohanty, A. K., & Misra, M. (2009). A study of dynamic mechanical and thermal behavior of starch/poly(vinylalcohol) based films. *Journal of Polymers and the Environment.*, *17*, 49–55.

Sarazin, P., Li, G., Orts, W. J., & Favis, B. D. (2008). Binary and ternary blends of polylactide, polycaprolactone and thermoplastic starch. *Polymer*, *49*, 599–609.

Shogren, R., Lawton, l., Tiefenbacher, J. W., & Chen, K. F. L. (1998). Starch–poly(vinyl alcohol) foamed articles prepared by a baking process. *Journal of Applied Polymer Science*, *68*, 2129–2140.

Sin, L. T., Rahman, W. A. W. A., Rahmat, A. R., & Samad, A. A. (2010). Computational modeling and experimental infrared spectroscopy of hydrogen bonding interactions in polyvinyl alcohol-starch bends. *Polymer*, *51*, 1206–1211.

Sreedhar, B., Chattopadhyay, D. K., Karunakar, M. S. H., & Sastry, A. R. K. (2006). Thermal and surface characterization of plasticized starch polyvinyl alcohol blends crosslinked with epicholohydrin. *Journal of Applied Polymer Science*, *101*, 25–34.

Sreedhar, B., Sairam, M., Chattopadhyay, D. K., Syamala Rathnam, P. A., & Mohan Rao, D. V. (2005). Thermal, mechanical, and surface characterization of starch–poly(vinyl alcohol) blends and borax-crosslinked films. *Journal of Applied Polymer Science*, *96*, 1313–1322.

Talja, R. A., Helen, H., Ross, Y. H., & Jouppila, K. (2007). Effect of various polyols and polyol contents on physical and mechanical properties of potato starch-based films. *Carbohydrate Polymers*, *67*, 288–295.

Tudorachi, N., Cascaval, C. N., Rusu, M., & Pruteanu, M. (2000). Testing of polyvinyl alcohol and starch mixtures as biodegradable polymeric materials. *Polymer Testing*, *19*, 785–799.

Viota, J. L., Lopez-Viota, M., Saake, B., Stana-Kleinschek, K., & Delgado, A. V. (2010). Organoclay particles as reinforcing agents in polysaccharide films. *Journal of Colloid and Interface Science*, *347*, 74–78.

Wang, Y., Li, D., Wang, L. J., Yang, L., & Ozkan, N. (2011). Dynamic mechanical properties of flaxseed gum based edible films. *Carbohydrate Polymers*, *86*, 499–504.

Wilhelm, H. M., Sierakowski, M. R., Souza, G. P., & Wypych, F. (2003). Starch films reinforced with mineral clay. *Carbohydrate Polymers*, *52*, 101–110.

Yan, R. X., & Tang, L. J. (2003). *Handbook of water soluble polymers* (1st ed.). Beijing: Chemical Industry Press.

Yao, K. H., Cai, J., Liu, M., Yu, Y., Xiong, H. G., Tang, S. W., et al. (2011). Structure and properties of starch/PVA/nano-SiO_2 hybrid films. *Carbohydrate Polymers*, *86*, 1784–1789.

Zhai, M. L., Yoshii, F., Kume, T., & Hashim, K. (2002). Syntheses of PVA/starch grafted hydrogels by irradiation. *Carbohydrate Polymers*, *50*, 295–303.

Zhang, Y. C., & Han, J. H. (2006). Mechanical and thermal characteristics of pea starch films plasticized with monosaccharides and polyols. *Journal of Food Science*, *71*, E109–E118.

Zhao, G. H., Liu, Y., Li, Y., Fang, C. L., Zhang, M., Zhou, C. Q., et al. (2006). Water resistance, mechanical properties and biodegradability of methylated-cornstarch/poly(vinyl alcohol) blend film. *Polymer Degradation and Stability*, *91*, 703–711.

Zhu, Z. F. (2003). Starch mono-phosphorylation for enhancing the stability of starch/PVA blend pastes for warp sizing. *Carbohydrate Polymers*, *54*, 115–118.