

Properties of polyvinyl alcohol/xylan composite films with citric acid



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ABSTRACT

Composite films of xylan and polyvinyl alcohol were produced with citric acid as a new plasticizer or a cross-linking agent. The effects of citric acid content and polyvinyl alcohol/xylan weight ratio on the mechanical properties, thermal stability, solubility, degree of swelling and water vapor permeability of the composite films were investigated. The intermolecular interactions and morphology of composite films were characterized by FTIR spectroscopy and SEM. The results indicated that polyvinyl alcohol/xylan composite films had good compatibility. With an increase in citric acid content from 10% to 50%, the tensile strength reduced from 35.1 to 11.6 MPa. However, the elongation at break increased sharply from 15.1% to 249.5%. The values of water vapor permeability ranged from 2.35 to 2.95×10^{-7} g/(mm² h). Interactions between xylan and polyvinyl alcohol in the presence of citric acid become stronger, which were caused by hydrogen bond and ester bond formation among the components during film forming.

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1. Introduction

Owing to their astatic appearance, light weight, low cost and ease in processing, plastic packaging materials are widely used in the food and preservation fields. However, they are dominated by petroleum-derived polymers. With depleting petroleum resources and increasing environmental concerns, chemically synthesized plastics lacking biodegradability are in direct conflict with the sustainable development needs (Mikkonen & Tenkanen, 2012). Therefore, utilizing biodegradable polymers such as polymers from nature to produce films becomes an inevitable trend in food packaging and technology development (Nakamura, Cordi, Almeida, Duran, & Mei, 2005; Prakash Maran, Sivakumar, Sridhar, & Prince Immanuel, 2013).

Usually films based on single biopolymers are highly sensitive to environmental conditions and generally possess low mechanical resistance (Kanatt, Rao, Chawla, & Sharma, 2012). Films can be produced by chemical cross-linking and physical blending. Polymer blending is an effective approach to endow new material with desired properties (Kanatt et al., 2012). Physically blending

biopolymers and synthetic polymers to achieve desired features has received increasing attention in recent years.

Hemicellulose has received an increasing interest especially in the last few decades for the production of biodegradable films and coatings (Hansen & Plackett, 2008; Mikkonen & Tenkanen, 2012). However, free-standing hemicellulose cannot form a continuous film, and several efforts (Goksu, Karamanlioglu, Bakir, Yilmaz & Yilmazer, 2007; Gröndahl, Eriksson, & Gatenholm, 2004; Peng, Ren, Zhong, & Sun, 2011; Saxena, Elder, Pan, & Ragauskas, 2009) have been made to overcome this drawback. One method is to add plasticizer into hemicellulose to enhance its film performance (Gröndahl et al., 2004). However, plasticizers can increase the elasticity of the film, and also lead to an increase in hydrophilicity. As a result, researchers have shifted to examining the films of hemicellulose with other polymers. Goksu et al. (2007) attempted to add lignin into xylan isolated from cotton stalks to produce a film for food packaging applications. The addition of 1% lignin into xylan solution was sufficient for the film formation. The elastic modulus and the hypothetical coating strength of the films obtained by using 8% xylan were 0.11 and 9.45 MPa, respectively. The addition of 7 wt% of sulfonated whiskers into the oat spelt xylan solution was found to increase the tensile energy absorption of xylan films by 445% and the tensile strength of the film by 141% (Saxena et al., 2009). Cellulose nanofibers (CNFs) were found to be a good nanoreinforcement to improve the mechanical properties of xylan films (Peng et al., 2011). At a CNF content of 20 wt%, the tensile stress and Young's modulus of the composite films increased up to 39.5 and 3404 MPa,

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respectively. Strong interactions could be formed between CNFs and xylan.

PVA is a representative water-soluble macromolecular resin and possesses better biodegradability than other resins. Furthermore, it has excellent film forming ability, and emulsifying and adhesive properties. As such, PVA has been used as a component in producing composite films by blending with other polymers from nature, for example PVA/wheat gluten (Dicharry et al., 2006), PVA/collagen hydrolysate (Alexy et al., 2003; Sarti & Scandola, 1995), PVA/chitosan (Kanatt et al., 2012; Naveen Kumar et al., 2010; Park, Jun, & Marsh, 2001), PVA/starch (Yang & Huang, 2008; Yun, Na, & Yoon, 2006), and PVA/carboxymethyl cellulose (Gupta, Agarwal, & Sarwar Alam, 2013). These composite films have potential applications in the packaging industry.

Xylan, as the main component of hemicellulose, has an abundance of hydroxyl groups distributed along the backbone and side chains, and is thus an ideal candidate for the formation of hydrogen bonds when blending with PVA. CA is an inexpensive, non-toxic food additive, which has been used as a cross-linking agent to improve the performance of starch (Ma, Chang, Yu, & Stumborg, 2009; Reddy & Yang, 2010; Shi et al., 2007), cellulose (Coma, Sebt, Pardon, Pichavant, & Deschamps, 2003), and PVA/starch (Shi et al., 2008) films. No information has been reported using CA as a plasticizer or cross-linking agent in PVA/xylan composite films to enhance the mechanical properties. The objective of this paper was to investigate the PVA/xylan composite films in the presence of CA. The impacts of the CA content and weight ratio of PVA and xylan on the mechanical properties, thermal stability, solubility, degree of swelling and water vapor permeability (WVP) of the composite films were comparatively analyzed. Intermolecular interactions and the phase compatibility between PVA and xylan in the composite films were studied by Fourier Transform Infrared (FTIR), and Scanning Electron Microscopy (SEM). Finally, the degree of degradation of the PVA/xylan composite films was examined.

2. Experimental

2.1. Materials

Xylan extracted from beech wood with over 90% residual units being xylose (M_w of 13,000 g/mol) and PVA with a degree of hydrolysis of 99% and a molecular weight average of 14,600–18,600 g/mol were purchased from Sigma Aldrich, USA. Both xylan and PVA were used without any further purification. CA, anhydrous CaCl_2 and NaCl were of analytical-reagent grade and bought from Guangzhou Chemical Reagent Factory, Guangzhou. Deionized water was used in all experiments.

2.2. Preparation of PVA/xylan composite films

Composite films were obtained by the casting method. A known weight of PVA was added in a single neck round bottom flask, and was stirred for 30 min at room temperature, then placed in a 95 °C oil bath. After 1 h, PVA formed a homogeneous solution. In succession, xylan and CA were added to the PVA solution at 95 °C and the mixture was stirred for 30 min. The final solution was kept at 75 °C for 4 h. Finally, the solution was poured into a teflon mould. Water was evaporated from the moulds in a ventilated oven at 50 °C overnight. In a typical experiment, the amount of CA was based on the total solids (PVA and xylan) content of the solution, ranged from 0% to 50%. These films obtained above were named non-cross linked films. Cross-linking PVA/xylan composite films were obtained after treating the above film in a hot air oven at 110 °C for 2.5 h. The dried non-cross linked and cross-linked films were stored in a desiccator for at least 48 h prior to all measurements.

2.3. Characterization

FTIR spectra were recorded with a Fourier transform spectrophotometer (Nicolet 750, Florida, USA) appended Attenuated Total Reflectance technique. The samples were thoroughly washed in water to remove unreacted CA, and then dried in an infrared drying oven. The spectra were obtained at a resolution of 4 cm^{-1} with 32 scans in the range from 4000 to 400 cm^{-1} .

Thermal analysis was performed using thermo gravimetric analysis on a simultaneous thermal analyzer (TGA Q500, TA Instruments, New Castle, USA). The composite film (9–11 mg) was cut into pieces and heated at a rate of 10 °C/min from room temperature to 700 °C. Moreover, nitrogen gas was purged at a flow rate of 20 mL/min.

The morphology of the surface and cross-section of the films was observed using a scanning electron microscope (SEM, Hitachi S-4300). The film was cut into smaller pieces, and was stuck on the sample stage by double-sided adhesive tape. For the cross-section of the films, the film was broken using liquid nitrogen, and stuck on the sample stage by double-sided adhesive. The samples were sputter-coated with thin a layer gold prior to the examination in order to make the films conductive. The test was operated in high-vacuum mode at an acceleration voltage of 15 kV.

2.4. Mechanical properties

Tensile testing was conducted on rectangular specimens with a width of 15 mm and a length of 150 mm which were prepared by a paper cutter (FQ-QZD15, Sichuan), using a tensile testing machine (Instron Universal Test Machine Model 5565) fitted with a 100 N load cell. The initial distance between the grips and the cross-head speed was kept constant at 50 mm and 10 mm/min, respectively. The measurements were performed at 23 °C and 50% relative humidity in a constant temperature and humidity chamber. The tensile strength (TS) and elongation at break (EAB) values of the PVA/xylan films were averaged over three specimens. The maximum load and the final extension at break were used for the calculation of TS and EAB, respectively.

2.5. Degree of swelling and solubility of PVA/xylan composite films

Pre-dried PVA/xylan composite films were cut into 2 × 2 cm^2 , immersed in 50-mL distilled water at room temperature (25 °C), and were soaked for 24 h. The moisture on the surface of the film was removed slightly by filter paper, and the weight of the films was measured. The degree of swelling (DS) (Yoon, Chough, & Park, 2007) in PVA/xylan composite film was calculated by Eq. (1).

$$DS = \frac{(W_1 - W_0)}{W_0} \quad (1)$$

where W_1 is the weight of PVA/xylan composite film when adsorption equilibrium is reached, g; W_0 is the pre-dry weight of PVA/xylan composite film, g.

Swelled PVA/xylan composite films were dried again for 24 h at 50 °C. And the solubility (S) (Yoon et al., 2007) was calculated by Eq. (2).

$$S = \frac{(W_0 - W_2)}{W_0} \quad (2)$$

where W_2 is the dry weight of the swelled PVA/xylan blend film, g.

2.6. Water vapor permeability

The water vapor permeability (WVP) of PVA/xylan composite films was measured according to an ASTM E96 method (ASTM,

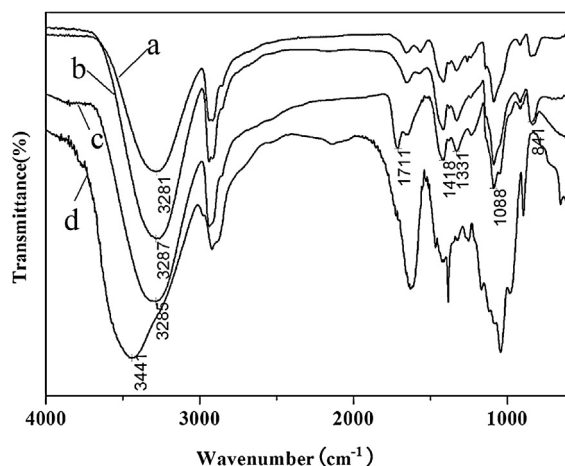


Fig. 1. FTIR spectra of PVA film (a), PVA/xylan composite film ((b) sample 6), PVA/xylan composite film with CA ((c) sample 8) and xylan (d).

1993). The sample was covered on the top of the bottle which completely filled with 3.0-g oven dry CaCl_2 to maintain 0% relative humidity, and sealed the films and bottle with Vaseline. The bottle was placed in a dryer at 25 °C and 75% relative humidity in the presence of saturated NaCl solution. The weight of the bottle was obtained at every 24 h interval. The WVP values were calculated by Eq. (3).

$$\text{WVP} = \frac{W_0}{(A \times d)} \quad (3)$$

where W_0 is the weight of PVA/xylan composite film, g; A is the area of the PVA/xylan composite film, cm^2 ; and d is the storage time, h.

2.7. Degree of degradation

The degree of degradation of the PVA/xylan films was determined by soil burial test. Selective pre-dried films (W_1) were cut into $30 \times 30 \text{ mm}^2$. In order to locate films after burial, the top of the films was covered by gauze. The films were buried 8 cm from the surface of the soil. After a certain time, the remaining piece after degradation was washed with water, and dried at 105 °C to a constant weight (W_2). The degree of degradation was calculated by Eq. (4).

$$\text{The degree of degradation} = \frac{(W_1 - W_2)}{W_1} \times 100\% \quad (4)$$

3. Results and discussion

3.1. Characteristics of composite PVA/xylan films

The compatibility of the PVA/xylan composite films and the interactions among PVA, xylan and CA were characterized by FTIR spectra and the result is shown in Fig. 1. The absorptions at 3450, 2933, 1414, 1043, 987 and 897 cm^{-1} are indicative of xylan (Fang, Sun, Tomkinson, & Fowler, 2000) (Fig. 1d). A characteristic absorption band occurs for pure PVA films at 1088 cm^{-1} which can be assigned to the C–O–C asymmetric stretching vibration (Fig. 1a).

In theory, the absorption of OH that is free from hydrogen bonding is around 3600 cm^{-1} , whereas the absorption band is shifted to a lower frequency due to stretching vibration if the intermolecular and intra-molecular hydrogen bonds are formed. As hydrogen bonding becomes stronger, O–H stretches appear at even lower frequencies. As seen in Fig. 1, O–H stretching vibration absorption band of xylan moves to a lower frequency when PVA is added into

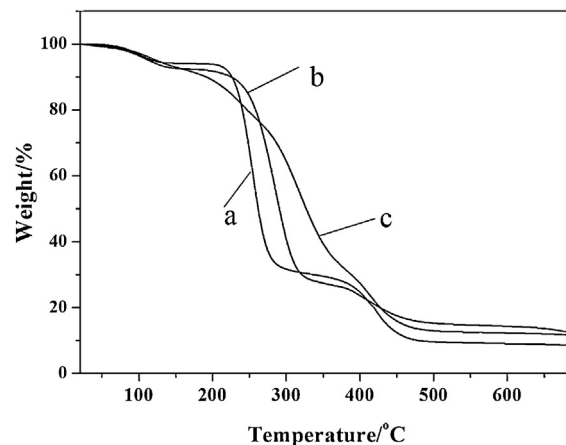


Fig. 2. TGA curves for PVA film (a), PVA/xylan composite film ((b) sample 6) and PVA/xylan composite film with CA ((c) sample 8).

the films, indicating the formation of hydrogen bonds between PVA and xylan.

Compared with spectra a and b, spectrum c exhibits a new absorption peak at 1711 cm^{-1} which corresponds to the typical C=O stretching vibration (Shi et al., 2007). This indicates that the esterification reaction occurred among CA, PVA and Xylan. Furthermore, the hydroxyl absorption band became stronger in the presence of CA (Fig. 1b and c), indicative of the enhanced hydrogen-bond interactions. The presence of hydrogen bond also shows a certain degree of compatibility of the two polymers. Thus, the compatibility of PVA/xylan polymers increased when CA is added in the composite films.

The effect of CA on the thermal stabilities of the PVA/xylan composite films was investigated by the TGA as shown in Fig. 2. The weight loss at about 100 °C was attributed to the evaporation of weakly physically and strongly chemically bound water for all curves. For curves a and b, it was found that the thermal degradation of PVA film and PVA/xylan composite films in the absence of CA displayed two main weight loss regions. The first region (230–380 °C) appeared due to the degradation of the side chain in the PVA matrix (Yang, Zhang, Yang, & Lu, 2012), such as the C–O bond. The weight loss on the second stage (390–460 °C) was attributed to the cleavage of C–C backbone in polymers, leading to so-called carbonization (Yang et al., 2012). However, when CA was added into the mixtures between PVA and xylan, the degradation boundaries were not clear. Thus, the addition of CA changed the thermal stability of the composite films.

The T_{onset} , T_1 , T_2 , T_3 and residual values of the composite films were determined from the DTG curves as shown in Table 1. There were increases in T_{onset} , T_1 , and T_2 of the PVA film after the addition of xylan, which could be attributed to the formation of hydrogen bonds between PVA and xylan, leading to an increase in the thermal stability. However, there are three maximum degradation peaks from curve c due to the decomposition of CA. CA has a DTG peak at 191 °C, with an 82.4 wt% loss in the TGA at 210 °C and a 93.5 wt% loss

Table 1
Thermal characteristic of TG curves in Fig. 2.

Curve	T_{onset} (°C)	T_1 (°C)	T_2 (°C)	T_3 (°C)	Residuals (wt%) at 600 °C
a	231.3	260.4	424.6	–	9.95
b	249.6	295.2	427.9	–	15.12
c	206.5	237.1	331.7	420.6	12.84

Note: the thermal decomposition temperature was taken as the onset of significant (5%) weight loss, after the initial moisture losses. T_1 , T_2 , T_3 was the maximum decomposition temperature of the first, second and third weight-loss step, respectively.

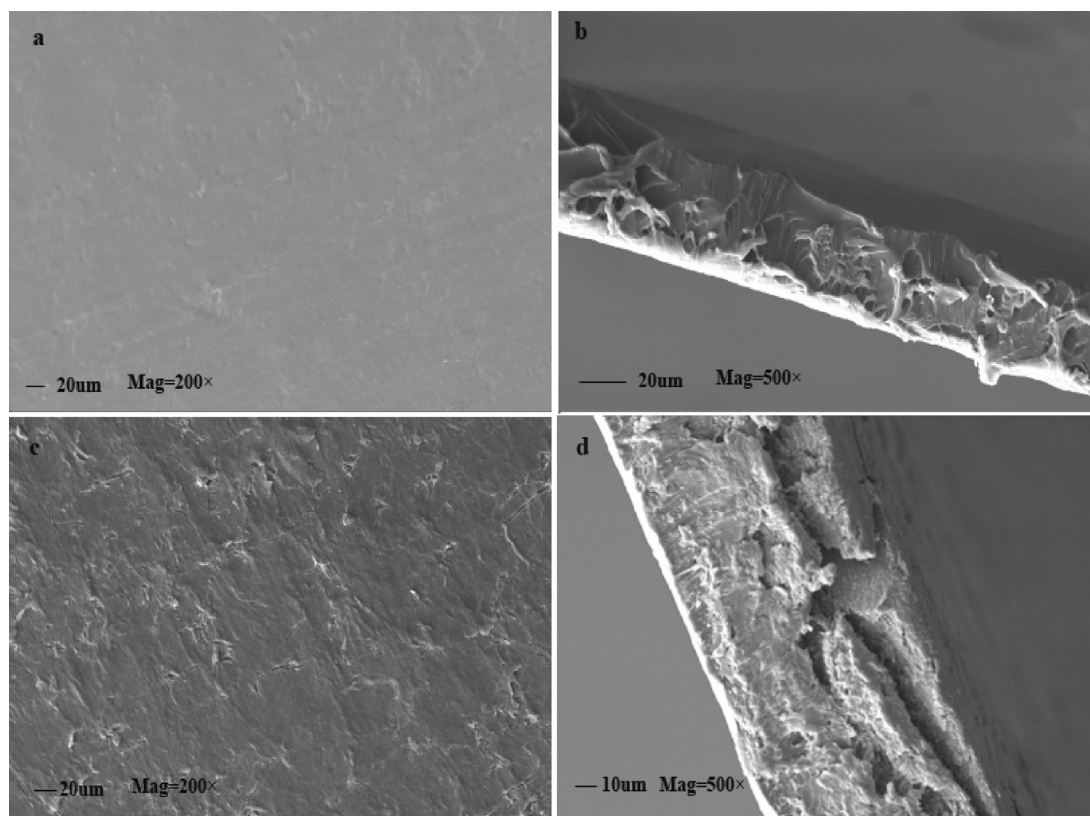


Fig. 3. SEM images of the surfaces ((a) and (c)) and cross-sections ((b) and (d)) of films. (PVA film, (a) and (b); the PVA/xylan composite film, sample 8, (c) and (d)).

at 600 °C (Salam, Pawlak, Venditti, & El-tahlawy, 2010; Wang et al., 2013). Residue of composite films at 600 °C was higher than that of the pure PVA films, which suggested that the thermal stability of the PVA matrix was enhanced by the addition of xylan and CA.

The SEM images of the surface and cross-section of selected films were shown in Fig. 3. The pure PVA film image displayed a dense smooth and homogeneous surface without pores or cracks. While the PVA/xylan composite films revealed a mesh structure, indicating the good dispersion and miscibility of xylan under the PVA matrix. Compared with the pure PVA film, the cross-section of the PVA/xylan composite films was compact. So the moisture was difficult to permeate, resulting in lower WVP. From the SEM images, no distinct separation of film matrix was observed in the PVA/xylan composite films due to the compatibility of the blend between PVA and xylan. The same conclusion was also reported by Limpan, Prodpran, Benjakul, and Prasarnpran (2012). They found that the cross-section of the fish myofibrillar protein (FMP)/PVA blend film was relatively rougher than PVA, and proved the compatibility of the blend components.

3.2. Mechanical properties

The influences of the weight ratio of PVA and xylan, CA content and reaction temperature on TS and EAB of the composite films were shown in Table 2. With an increase in the weight ratio of PVA and xylan, TS was enhanced while EAB sharply increased (sample 1 to 5). The blend of PVA contributed to the improved mechanical properties of the composite films. Compared to sample 4, TS slightly decreased and EAB reached the maximum value for sample 5, which was almost two times that of sample 4. At a PVA/xylan weight ratio of 3.0, the composite films had great flexibility.

Mechanical properties are related to the weight ratio of the original materials as well as to the content of CA. Generally, TS increased and EAB decreased as the percentage of the cross-linker

increased. The opposite trend occurred when the amount of the plasticizer increased (Shi et al., 2008). The effect of CA on TS and EAB was examined comparatively, which were seen in samples 5–9 of Table 2. As the CA content was increased, the values of TS, firstly increased slightly and then decreased while the values of EAB sharply increased, indicating that CA mainly acted as a plasticizer in the solution at a reaction temperature of 75 °C. With an increase in CA concentration from 10% to 50%, TS reduced from 35.1 to 11.6 MPa. However, EAB increased sharply from 15.1% to 249.5%. As a plasticizer, CA increases the interstitial volume of the material or the macromolecular mobility of the polymer, and consequently, the polymeric networks become less dense due to the decrease in intermolecular forces. Thus the extensibility and flexibility of the films are improved (Sothornvit & Krochta, 2000). A few studies (Coma et al., 2003; Ma et al., 2009; Reddy & Yang, 2010; Salam et al., 2010; Shi et al., 2007) have shown that CA acts as a cross-linking agent above 100 °C at the drying conditions. At 75 °C, CA dehydrated to lose one water molecule forming an ester bond with either PVA or xylan, which was confirmed in spectrum c in Fig. 1.

To ensure the occurrence of the cross-linking reaction in the composite solution, a reaction temperature of 110 °C was applied in this work, and the corresponding samples 10–13 were produced in Table 2. At the same CA content, the values of TS synthesized at 110 °C were clearly higher than those prepared at 75 °C, but the opposite trend appeared on the values of EAB of the films. This is may be due to the interconnection of the component molecules in the films by cross-linking, which could increase the molecular weight of the components and also provides better intermolecular interactions between molecules, leading to higher tensile strength (Reddy & Yang, 2010), as compared to samples 5–8. When the CA content was 10%, the maximum value of TS was achieved at 49.3 MPa while with the lowest value of EAB at 6.8%. At a high content of CA, excess amount act as a plasticizer leading to a lower TS

Table 2
Influences of reaction conditions on mechanical properties and WVP.

Sample	The ratio ^a	CA content (%)	RT ^b (°C)	TS (MPa)	EAB (%)	WVP (g/(mm ² h) × 10 ⁻⁷)
1	1	50	75	7.6	35.5	2.48
2	1.5	50	75	8.8	22.7	2.50
3	2	50	75	12.7	92.9	2.49
4	4	50	75	15.2	136.7	2.35
5	3	50	75	11.6	249.5	2.40
6	3	0	75	30.3	10.7	2.95
7	3	10	75	35.1	15.1	2.59
8	3	20	75	20.3	85.2	2.71
9	3	30	75	14.5	165.4	2.48
10	3	0	110	46.4	5.8	–
11	3	10	110	49.3	6.8	–
12	3	20	110	38.1	9.2	–
13	3	30	110	32.6	9.5	–

^a The weight ratio of PVA and xylan.

^b Abbreviation for reaction temperature.

and a higher EAB. Lower EAB (<10%) restricts the commercial application of the composite films, and thus the cross-linking composite films at high CA content were no longer studied although higher TS was achieved.

3.3. Solubility and degree of swelling of PVA/xylan composite films

The solubility and the degree of swelling (DS) are the most important properties for food packaging. Usually DS decreased as the degrees of esterification and cross-linking were increased (Zou, Qu, & Zou, 2007). DS and solubility are functions of PVA/xylan weight ratio and CA content as displayed in Fig. 4. With an increase in the PVA/xylan weight ratio, DS firstly increased and then

decreased, and the opposite trend occurred in the solubility. This may be explained that an increase in the xylan content presented more carboxyl groups in xylan that could form ester bonds with CA, consequentially leading to an increase in the solubility. PVA is not easily dissolved into water at room temperature. The hydroxyl groups on the chain of PVA and xylan endowed the composite films with the water-swollen capacity. And with an increase in the PVA content, DS increased, which was due to more hydrophilic groups present on the high molecular weight PVA.

With an increase in the CA content, DS of the PVA/xylan composite films decreased while the solubility increased slightly. This is possibly due to the formation of hydrogen bonds between PVA and xylan, leading to the interstitial volume decrease (Yun et al., 2006), or excess CA interspersed into the PVA and xylan molecular interstitial space and formation of hydrogen bonds between PVA and xylan molecules. At the same time, the excess CA reacted with xylan to form soluble polymers, resulting in a higher solubility.

3.4. Water vapor permeability (WVP)

One of the main functions for a food packaging film is to restrain moisture migration between the food components and the environment. Lower permeability is better for food packaging films. WVP as the indicator of film properties was applied to our work. WVP values obtained for the PVA/xylan composite films were shown in Table 2. At the same weight ratio of PVA/xylan was 3:1, an increase in the CA content led to a decrease in the WVP values. It is suggested that the addition of CA can reduce the moisture permeability of the PVA and xylan composite films. When the CA content was 50%, the minimum value of WVP at 2.40×10^{-7} g/(mm² h) was obtained because esterification occurred and esterification could enhance the water resistance which corresponded to a lower solubility of the blend films. When varying the weight ratio of PVA/xylan, only small changes were seen in the WVP values. Thus, the weight ratio of PVA/xylan had little effect on the WVP values.

3.5. Degree of degradation

To test the degree of degradation of PVA/xylan composite films for their potential applications in industry, the soil burial testing method was used in this work. The results of the degree of degradation of PVA/xylan composite films were illustrated in Fig. 5. It was found that the degree of degradation of the films was continuously enhanced within 30 days. After 30 days, the surface of the film showed white regions, which is indicative of microbial attacks. Clearly, the components of the composite films greatly impacted the degree of degradation. The degree of degradation of the film containing 50% xylan (sample 1) was relatively higher than that

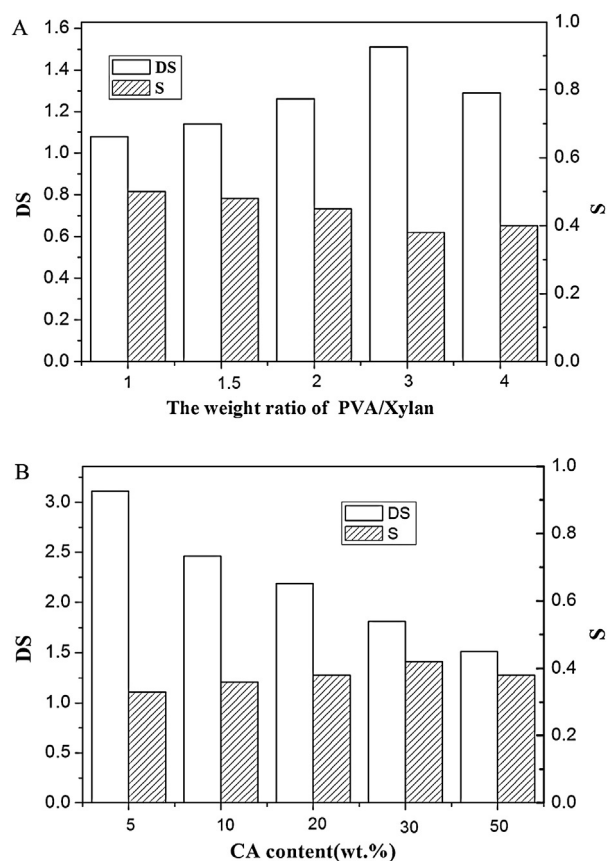


Fig. 4. The effects of the PVA/xylan weight ratio ((A) CA content of 50%) and the CA contents ((B) the PVA/xylan weight ratio of 3.0) on the solubility and DS of the PVA/xylan composite films.

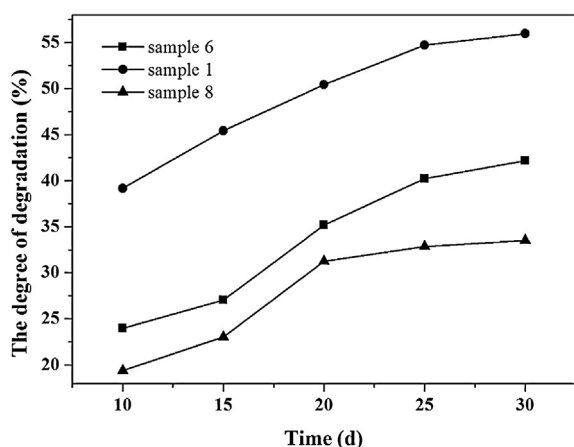


Fig. 5. The degree of degradation of the composite PVA/xylan films (samples 1, 6, and 8).

containing 25% xylan (sample 6 and 8). This may be due to xylan was more susceptible to microbial attack, and the maximum value of the degree of degradation for samples 1, 6 and 8 were 56.0%, 42.2% and 33.5%, respectively, at 30 days. From samples 6 and 8, the results indicated that the composite films without CA had a higher degree of degradation than composite films containing CA. This phenomenon may be attributed to the ester bonds. However, in the absence of CA, PVA and xylan formed hydrogen bonds. Microorganism immersed into the network could easily attack hydrogen bonds.

4. Conclusion

In summary, the PVA/xylan composite films were prepared with solution and mixing, followed by film casting in the presence of citric acid. Utilization of PVA in composites films led to a significant enhancement in mechanical properties. Improved tensile strength and elongation properties could be achieved by changing the PVA/xylan weight ratio and CA content. Increasing CA content caused a reduction in TS but an enhancement in flexibility, thereby EAB values were increased. CA as a cross-linking agent led to high TS but low EAB. CA content had a significant impact on the moisture permeability but the PVA/xylan weight ratio had little effects. These results clearly showed that CA content in film formulations had significant effects on the mechanical properties, DS and moisture permeability. Moreover, a higher xylan content resulted in a higher degree of degradation. At the same PVA/xylan weight ratio, the composite film without CA had a higher degree of degradation than that with CA. Due to the biodegradability of PVA and xylan, the composite films can replace the petroleum derived products, and possess potential in agriculture and food packaging.

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