International Journal of Biological Macromolecules xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

Studies of the plasticizing effect of different hydrophilic inorganic salts on starch/poly (vinyl alcohol) films

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ARTICLE INFO

Article history:
Received 10 June 2015
Received in revised form 5 November 2015
Accepted 16 November 2015
Available online xxx

Keywords:
Starch
Poly (vinyl alcohol)
Inorganic salt

ABSTRACT

The effects of different inorganic salts LiCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, and $AlCl_3 \cdot 6H_2O$ on the crystalline, thermal, water vapor barrier, and tensile properties of starch/PVA films were studied. The high plasticizing efficiency of all these four inorganic salts for starch/PVA film was confirmed by the obtained results. These four salts all had a good compatibility with starch/PVA within the content of 15 wt% and starch/PVA became completely miscible with the addition of 15 wt% inorganic salts. All these four salts had a strong destroying effect on the crystals of starch and PVA. Among these four salts, $AlCl_3 \cdot 6H_2O$ had the largest negative effect on the thermal stability of starch/PVA and LiCl had the largest improving effect on the water sorption rate of starch/PVA film. On the whole $MgCl_2 \cdot 6H_2O$ and $CaCl_2$ were the more suitable plasticizer for starch/PVA film among these four inorganic salts. With the addition of 15 wt% $MgCl_2 \cdot 6H_2O$ and $CaCl_2$, the elongation at break of starch/PVA film could reach to 418.83% and 434.80%, respectively.

1. Introduction

Starch is one of the most promising natural polymeric materials that can be used to replace the polymeric materials made from petroleum for its low cost and high performances [1,2]. Moreover, the biodegradable plastics with high mechanical properties and processability properties could be obtained from the blends of starch and other biodegradable polymers, e.g., chitosan, gelatin, poly (lactic acid) (PLA) [3,4], polycaprolactone (PCL) [5–7], and poly (vinyl alcohol) (PVA). PVA is one of the most important synthetic polymers which can be produced via a non-petroleum route [8] and PVA is often used to form the blend with natural polymers to prepare the biodegradable plastics. Recently the starch/PVA blend has attracted more and more attention for its high performance and starch/PVA blend plastics have been one of the most popular biodegradable plastics widely used in packaging and agricultural applications [9–20].

However, both starch and PVA have many hydroxyl groups on the chains and the hydroxyl groups would easily form the hydrogen bonding. This makes the pure starch/PVA film brittle and easy to break during preparation and application processes [21,22]. The poor mechanical properties have restricted the development of starch/PVA materials. Thus the improving of mechanical properties of starch/PVA blend is necessary. Adding the plasticizer is the most simple and commonly used way. The most commonly used plasticizer for starch/PVA is the polyols such as glycerol, ethylene glycol, and poly (ethylene glycol) [23–29]. These plasticizers can form interaction with the hydroxyl groups of starch and PVA chains and destroy the intermolecular hydrogen bonding between starch and PVA itself chains. However, the plasticizing efficiency of these existing plasticizers is not high enough for some applications, such as the melt processing of starch and PVA. The exploiting of new and high efficient plasticizer for starch/PVA blend is important and more and more researches have focused on this. Except the small organic molecule, many kinds of inorganic salts were also doped into starch and PVA [30–35]. It was interesting to find that many positive and negative ions could form interaction with the hydroxyl groups of starch and PVA chains. The inorganic salts would restrain the recrystallization and decrease the crystallinity of starch and PVA via this interaction. Moreover, when the inorganic salts were hydrophilic and the incorporation of these salts would lead to the increase of the water sorption rate of starch and PVA, these inorganic salts usually could also act as the plasticizer for starch and PVA. Moreover, the compatibility between the inorganic salts and polymer was good and the high plasticizing efficiency of $Mg(NO_3)_2 \cdot 6H_2O$ on PVA was confirmed [13]. Abbott et al. employed choline chloride/glycerol as the plasticizer for starch and proved that choline chloride/glycerol could be comparable to glycerol and sorbitol as a potential plasticizer for starch [36,37]. These researches indicated that the inorganic salt may be the suitable plasticizer of the starch/PVA blends.

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http://dx.doi.org/10.1016/j.ijbiomac.2015.11.046
0141-8130/

The aim of this paper was to study the effects of four different inorganic salts LiCl, $MgCl_2{\cdot}6H_2O$, $CaCl_2$, and $AlCl_3{\cdot}6H_2O$ on the crystalline, thermal, water barrier properties, and tensile properties of starch/PVA films to select the suitable inorganic plasticizer for starch/PVA film. It could be expected that the scope of the plasticizers of starch and starch based materials would be enlarged from this study.

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). LiCl was pursed from Aladdin chemical reagent. $CaCl_2$, $MgCl_2{\cdot}6H_2O$ and $AlCl_3{\cdot}6H_2O$ was purchased from Kelong chemical Co. (Chengdu, China). Distilled water was used throughout the experiment.

Starch/PVA films were prepared by the casting method. First, 3.5 g starch, 1.5 g PVA and a calculated amount of inorganic salts (LiCl, $CaCl_2$, $MgCl_2{\cdot}6H_2O$, and $AlCl_3{\cdot}6H_2O$) were dissolved in distilled water by heating in an oil bath at 95 °C for 2 h, and the 5 wt% starch/PVA aqueous solutions were prepared, which was called the film-forming solution. The film-forming solutions were casted onto the petri-dish and dried at 60 °C for 12 h to completely eliminate water. Dried films were put into polyethylene bags and stored at relative humidity (RH) of 54% for one week before testing. The experimental ingredients used to prepare the films and the nomenclatures used for each sample are shown in Table 1. For comparison, the crystal water weight of the inorganic salts was eliminated to ensure the same salt content was added. Finally, 5 wt%, 10 wt%, and 15 wt% LiCl, $MgCl_2$, $CaCl_2$, and $AlCl_3$ plasticized starch/PVA films were prepared as shown in Table 1.

2.2. Film thickness

The film thickness was measured at six random positions with a vernier caliper to the nearest 0.001 mm. The average value for each film was used to calculate its tensile properties and water vapor permeability.

2.3. Scanning electron microscope (SEM)

The cross section of the starch/PVA films was observed on a mini-Inspect SEM instrument (HIROX SH-4000 M, China). The cross sections were first vacuum coated with gold and examined with the acceleration voltage of 20 kV.

2.4. Water content

The water sorption properties of the films at the RH of 33%, 54%, 76%, and 100% were determined by thermogravimetric method. The films were firstly stored at the corresponding relative humidity for one week and then dried at 100 °C for 12 h. The water content (WC) was calculated as the following equation.

$$WC = \frac{W_e - W_d}{W_d} 100\%$$

W_e was the weight of the films after storing at corresponding RH for one week, W_d was the weight of the films after drying at 100 °C for 12 h. The RH of 33%, 54%, 76%, and 100% was obtained in the vacuum desiccator over saturated salt solutions of $MgCl_2$, $Mg(NO_3)_2$, NaCl, and distilled water at 24.8 ± 0.2 °C, respectively.

2.5. X-ray diffraction (XRD)

X-ray diffraction patterns were recorded in the reflection mode in the angular range of 5°–50° (2θ) at ambient temperature by an X'Pert Pro MPD diffractometer (Phillips). The radiation from the anode, operating at 50 kV and 35 mA, was monochromized with a nickel foil. The measurements were performed at a scanning speed of $2\theta = 0.06° s^{-1}$.

2.6. Differential scanning calorimetry (DSC)

The DSC measurements were performed by a differential scanning calorimeter (TA Q2000). Slices of the modified starch/PVA films with total weight of 5–7 mg were weighted and sealed in aluminum pans. The pans were heated from −80 °C to 80 °C at a rate of 10 °C/min under a flow of Nitrogen.

2.7. Thermal gravity analysis (TGA)

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

2.8. Tensile testing

The tensile strength and elongation at break of starch/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. Samples were equilibrated in vacuum desiccators over the saturated solution of $Mg(NO_3)_2$ giving RH of 54% for one week before tensile testing. The data were the average of 5–7 specimens.

Table 1
Experimental ingredients and nomenclatures of films.

Sample	Starch (g)	PVA (g)	LiCl (g)	$MgCl_2{\cdot}6H_2O$ (g)	$CaCl_2$ (g)	$AlCl_3{\cdot}6H_2O$ (g)
SP	3.5	1.5				
SPL05	3.5	1.5	0.25			
SPL10	3.5	1.5	0.50			
SPL15	3.5	1.5	0.75			
SPM05	3.5	1.5		0.53		
SPM10	3.5	1.5		1.06		
SPM15	3.5	1.5		1.59		
SPC05	3.5	1.5			0.25	
SPC10	3.5	1.5			0.50	
SPC15	3.5	1.5			0.75	
SPA05	3.5	1.5				0.45
SPA10	3.5	1.5				0.90
SPA15	3.5	1.5				1.35

Please cite this article in press as: X. Jiang, et al., Int. J. Biol. Macromol. (2015), http://dx.doi.org/10.1016/j.ijbiomac.2015.11.046