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Preparation and properties of plasticized starch modified with poly(ε-caprolactone) based waterborne polyurethane

Xiaodong Cao [a], Peter R. Chang [a,*], Michel A. Huneault [b]

[a] *Bioproducts and Bioprocesses National Program, Agriculture and Agri-Food Canada, 107 Science Place, Saskatoon, Sask., Canada S7N 0X2*
[b] *Industrial Materials Institute, National Research Council Canada, 75, de Mortagne, Boucherville, Que., Canada J4B 6Y4*

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Abstract

Biodegradable blends were prepared successfully from plasticized starch (PS) and poly(ε-caprolactone)-based waterborne polyurethane (WPU) by casting and evaporation. The morphology, thermal behaviour, and mechanical properties of the films were investigated by means of wide-angle X-ray diffraction, differential scanning calorimetry, scanning electron microscopy, and tests of mechanical properties and water absorption. The results indicated that the blends had a good miscibility while the WPU content was lower than 20 wt% due to the hydrogen bonding interactions between the carboxyl, carbonyl, urethane groups of WPU and hydroxyl groups of starch, whereas the phase separation occurred with an increase of WPU content. Compared with pure PS, the tensile strength of the blend containing 10 wt% of WPU increased from 2.93 to 3.89 MPa. Moreover, the elongation at break of the blends significantly increased from 35% to 886% with WPU content increased from 0 to 50 wt%. It is worth noting that the water uptake of the PS/WPU blends also decreased because the presence of WPU in the PS matrix. Therefore, the WPU played an important role in improving the mechanical properties, and water resistance of the starch-based material.

Keywords: Starch; Waterborne polyurethane; Poly(ε-caprolactone); Modification

1. Introduction

Development of biodegradable plastics has been considered to be an ultimate solution to the environmental problem caused by the disposal of non-biodegradable plastic wastes. Up to date, however, most of the biodegradable polymers cannot be used widely because of their economic and other considerations (Choi, Kim, & Park, 1999). So there is an urgent need to develop new biodegradable materials that have comparable properties with current polymeric materials at an equivalent cost. Among the many known biodegradable polymers, starch is one of the most promising materials for biodegradable plastics because of the abundant supply, low cost, renewability, biodegradability, and ease of chemical modifications (Choi et al., 1999; Mathew & Dufresne, 2002; Mohanty, Misra, & Hinrichsen, 2000). Incorporating plasticizers, such as water and/or polyalcohols, starch takes on thermoplastic properties and is called thermoplastic starch (TPS) or plasticized starch (PS) using technology already developed for the production of synthetic plastics (Carvalho, Job, Alves, Curvelo, & Gandini, 2003; Gaudin, Lourdin, Forssell, & Colonna, 2000). In recent years, TPS or PS has attracted considerable attention and has offered an interesting alternative for synthetic polymers where long-term durability is not needed and rapid degradation is an advantage (Van Soest, Benes, DeWit, & Vliegenthart, 1996). However, compared to conventional synthetic thermoplastics, biodegradable products based on starch, unfortunately, still exhibit many disadvantages, such as water sensitivity, brittleness, and poor mechanical properties (Santayanon & Wootthikanokkhan, 2003). Various physical or chemical means have been used to solve these problems, including blending

* Corresponding author. Tel.: +1 306 9567637; fax: +1 306 9567247.
E-mail address: Changp@agr.gc.ca (P.R. Chang).

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with other synthetic polymers (Dufresne & Vignon, 1998), the chemical modification (Sagar & Merrill, 1995), graft copolymerisation (Suda, Kanlaya, & Manit, 2002), and incorporating fillers such as lignin (Lepifre et al., 2004), fibres or crystallines (Curvelo, De Carvalho, & Agnelli, 2001; De Carvalho, Curvelo, & Agnelli, 2002; Lu, Weng, & Cao, 2005c, 2005d; Soykeabkaew, Supaphol, & Rujiravanit, 2004), tunicin whiskers (Angles & Dufresne, 2000, 2001), and clay (Wilhelm, Sierakowski, Souza, & Wypych, 2003; Chen & Evans, 2005). Nevertheless, blending with biodegradable synthetic polymers offers a relative simple and effective route to prepare starch based biodegradable materials with enhanced properties.

The ability to have different types of molecular architectures specifically designed for each application has made polyurethane (PU) one of the most popular polymers used in a variety of products, such as coatings, adhesives, flexible and rigid foams, elastomers, tough solids, and so forth (Li, Vatanparast, & Lemmetyinen, 2000). PU has been gradually replaced by the waterborne polyurethanes (WPU) due to health and environmental concerns (Chan & Chen, 1993; Dreja, Heine, Tieke, & Junkers, 1997; Kim & Kim, 1991; Wicks, Wicks, & Rosthauser, 2002). WPU has many features of conventional organic solvent-borne PU with the advantages of low viscosity at high molecular weight, low toxicity, and good applicability (Kuan et al., 2005). In particular, polyester-type WPU showed completely biodegradable because of its hydrolytic character (Furukawa, 1997; Pegoretti, Fambri, Penati, & Kolarik, 1998). Therefore, the biodegradable WPU is a good candidate to blend with starch to prepare biodegradable blends (Cao, Zhang, Huang, Yang, & Wang, 2003; Wu & Zhang, 2001). For instance, Lu et al. (Lu, Tighzert, Berzin, & Rondot, 2005a, 2005b) used WPU prepared from natural materials such as castor oil and rapeseed oil to enhance the performances of the TPS successfully. In the past decade, blends of starch/poly(ε-caprolactone) (PCL) have attracted much attention because PCL is a high flexible, biodegradable, hydrophobic, and commercially available biodegradable polymer (Carioca, Arora, Selvam, Tavares, & Kennedy, 1996; Koenig & Huang, 1995). However, the main limitation of starch/PCL is due to a lack of adhesion between starch and PCL owing to their different polarity. Poor mechanical properties are apparent if the starch content is high (Avella et al., 2000). Introducing a reactive functional group on the PCL or starch phase, and adding compatibilizers in the blends both have been used to improve the compatibility (Avella et al., 2000; Choi et al., 1999; De Carvalho, Curvelo, & Agnelli, 2001; Mani, Tang, & Bhattacharya, 1998). In present work, we attempt to use PCL as soft segment material to synthesize a WPU containing hydrophilic groups, which can improve the adhesion with starch during the blending processing. A series of biodegradable films of PS/WPU with WPU content ranging from 10 to 50 wt% were prepared by solution casting and evaporation. The effects of WPU content on the morphology, mechanical properties, and water sensitivity were investigated by scanning electron microscopy (SEM), wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and testing of mechanical properties and water absorption.

2. Experimental

2.1. Materials

Pea starch composed of 35% amylose and 65% amylopectin, and with average particle size of about 29 μm, was supplied by Nutri-Pea Limited Canada (Portage la Prairie, Canada). PCL diol ($M_n = 1250$), isophorone diisocyanate (IPDI), 2,2-bis(hydroxymethyl) propionic acid (DMPA), triethylamine (TEA), acetone, and glycerol (99.5% purity) were purchased from Sigma–Aldrich Canada Ltd. (Oakville, Canada) and used as received without further purification.

2.2. Synthesis of waterborne polyurethane dispersion

The WPU dispersion was prepared using PCL diol with some modifications from previous method (Lu et al., 2005a, Lu, Tighzert, Dole, & Erre, 2005b) as following. PCL diol (60 g), and DMPA (4.02 g) were introduced into a four-necked flask equipped with mechanical stirrer, condenser and thermometer, and then the mixture was heated up to 85 °C until the PCL diol melted completely. IPDI (24.6 g) was added dropwise and the reaction was carried out under a dry nitrogen atmosphere for 4 h. Subsequently, about 80 mL of acetone was poured into the flask to reduce the viscosity of prepolymer and then maintained at 60 °C. After neutralization with TEA (3.01 g) for 30 min, the resulting solution was dispersed with distilled water under vigorous stirring. After stirring at room temperature overnight, acetone in the WPU dispersion was removed by rotary vacuum evaporation at 30 °C. The final solid content was of 28 wt%.

2.3. Preparation of the PS/WPU films

Fabrication of PS/WPU films was based on a convenient solution process. Starch and glycerol were mixed and dispersed in distilled water. The mixture contained 7.0 wt% pea starch, 3.0 wt% glycerol, and 90 wt% water. Then it was charged into a round bottom flask equipped with stirrer and heated at 100 °C for 20 min until the mixture gelatinized. Subsequently, the desired weight of WPU dispersion was added and stirred for another 20 min. After degassing under vacuum and cooling to 70 °C, the mixture was cast in a polystyrene Petri dish and dried at 40 °C. By changing the WPU content of 10, 20, 30, 40, and 50 wt%, a series of PS/WPU films with a thickness of about 0.3 mm were prepared. They were coded as SU-10, SU-20, SU-30, SU-40, and SU-50, respectively. The WPU content was expressed on water-free PS matrix. As a control, a PS film without addition of WPU and a pure WPU film were

obtained using the same fabrication process, respectively. Before various characterizations, the resulting films were kept at room temperature in a conditioning desiccator of 43% relative humidity (RH) for at least one week to ensure equilibration of water content in the films.

2.4. Characterizations

A scanning electron microscope (SEM, S-570, Hitachi, Japan) was used to observe the morphology of the PS and PS/WPU films. The films were frozen in liquid nitrogen and snapped immediately, and then the cross-sections of the films were coated with gold and observed with an accelerating voltage of 20 kV.

Differential scanning calorimetry (DSC) measurement of the films was carried out on a DSC200 PC apparatus (Netzsch Co., Germany) with a cooler system of liquid nitrogen. Conditioned samples were placed in hermetic cells and at least two individual measurements were carried out to ensure the reliability. Each sample was heated from −80 to 250 °C at a heating rate of 10 °C/min. In this case, the melting temperature (T_m) was taken as the peak temperature of the melting endotherm. The heat of fusion (ΔH_m), calculated from the areas of the melting endotherm, was the ratio of the apparent enthalpy and of the weight fraction of the starch in the blends.

Wide-angle X-ray diffraction patterns were recorded on an X-ray diffraction instrument (XRD-6000, Shimadzu, Tokyo, Japan), using CuK_α radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA with a scan rate of 4°/min. The diffraction angle ranged from 4° to 40°.

The tensile strength and elongation at break of the films were measured on a universal testing machine (CMT 6503, Shenzhen SANS Test Machine Co. Ltd., China) at room temperature with gauge length of 5 cm and crosshead speed of 10 mm/min. An average value of at least five replicates for each sample was taken.

The kinetics of water absorption was determined for all blends. The samples used were thin rectangular strips with dimension of 50 mm × 10 mm × 0.3 mm. The samples were vacuum-dried at 80 °C overnight and kept at 0% RH (P_2O_5) for one week. After weighting, they were conditioned at room temperature in a desiccator of 98% RH ($CuSO_4{\cdot}5H_2O$ saturated solution). The conditioning of samples in high moisture atmosphere was preferred to the classical technique of immersion in water, because starch is very sensitive to water and can partially dissolve after long-term exposure to water (Angles & Dufresne, 2000). The samples were removed at specific intervals and weighed until the equilibrium state was reached. The water uptake (WU) of the samples was calculated as follows:

$$\mathrm{WU}\ (\%) = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

where W_0 and W_t were the weights of the sample before exposure to 98% RH and after t h exposure to 98% RH.

3. Results and discussion

3.1. Morphology and structure of the PS/WPU films

The SEM photographs of the fractured surfaces of PS and PS/WPU blends are shown in Fig. 1. As shown in Fig. 1a, the surface of the PS matrix without an addition of WPU is rather smooth except for some of bright strips resulted from the electron susceptibility of starch matrix, implying the granules of starch are destroyed completely and form a homogeneous structure. The blends of SU-10 and SU-20 also exhibited a relatively smooth fracture surface, indicating a high compatibility between PS and WPU or a very good and uniform dispersion of WPU in the PS matrix with strong interfacial adhesion. With an increase of WPU content, the fracture surfaces became rougher on the images of SU-30 and SU-50. It demonstrated that the PS and the WPU are immiscible when the content of WPU in the blends was higher than 30 wt%. However, an absence of cavities or voids meant good adhesion between the two phases. This could be attributed to the hydrophilicity of both WPU and PS and the hydrogen bonding interactions between them. The WPU possesses carboxylic, carbonyl, urethane groups and PS has abundant hydroxyl groups. These interactions lead to lowering the interfacial tension between the PS and the WPU phases, and offer a certain degree of compatibility (Shin, Lee, Shin, Balakrishnan, & Narayan, 2004).

The PS/WPU blends resulting from casting and evaporation were studied by WAXD as a function of the WPU content and the corresponding diffractograms are shown in Fig. 2. For PS film, the typical C-type crystallinity pattern with peaks at $2\theta = 5.6°$ (characteristic of B type polymorphs), 15.0° (characteristic of A type polymorphs), 17.0° (characteristic of both A and B type polymorphs), 20.1° and 22.5° (characteristic of B type polymorphs) were observed clearly (Rindlava, Hulleman, & Gatenholma, 1997). The crystalline structure resulting from spontaneous recrystallization or retrogradation of starch molecules after melting or gelatinization has frequently been detected in food and thermoplastic materials (Souza Rosa & Andrade, 2004). In addition, PCL is a kind of semi-crystalline thermoplastic polymer with characteristic peaks at $2\theta = 21.5°$, 22°, and 23.5° (Sarasam, Krishnaswamy, & Madihally, 2006). For pure WPU, however, only a broad diffraction hump at $2\theta = 19.5°$ could be observed, indicating the amorphous nature of the film. It can be explained by the fact that the polyurethane prepared with PCL as soft-segments, when the M_n of PCL diol is lower than a value of around 2000, usually shows no crystallinity because the PCL molecular chain length is not long enough for chain folding (Heijkants et al., 2005b; Ping, Wang, Chen, & Jing, 2005). Addition of WPU did not significantly affect the crystalline structure of the PS matrix, as supported by the observation that the WAXD patterns of the PS/WPU blends still keep the characteristic peaks of pea starch except the intensity decrease with increasing WPU content.

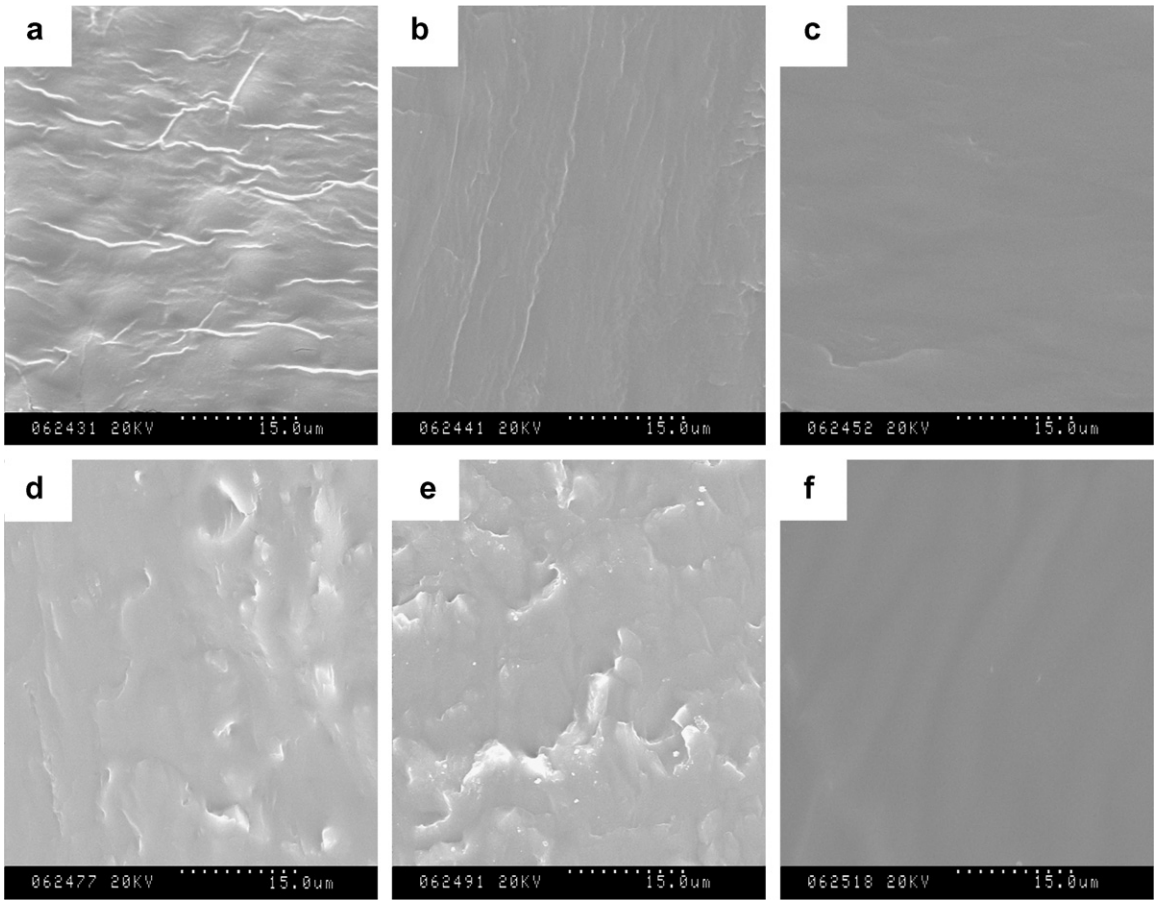

Fig. 1. SEM images of the PS/WPU blends with different WPU content: a, 0 wt%; b, 10 wt%; c, 20 wt%; d, 30 wt%; e, 50 wt%; f, 100 wt% (scale bar: 15.0 μm).

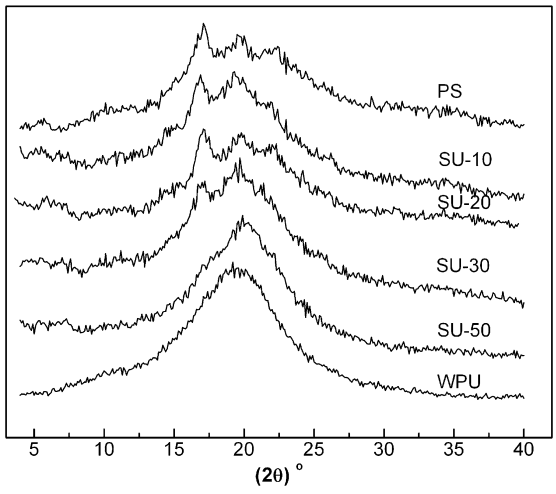

Fig. 2. WAXD patterns of PS, WPU, and PS/WPU blends.

Simultaneously, there was no evidence of any additional peak in the diffractograms. Therefore, it can be concluded that the diffractograms of blends are only superimpositions of the diffractograms of the two components, i.e. the amorphous nature of WPU and the crystal structure of PS are unchanged.

3.2. Thermal properties

To further understand the structure and interaction between the two components, DSC studies of the PS and PS/WPU blends were performed. Their DSC thermograms are shown in Fig. 3, and the corresponding data are collected in Table 1. Similar to the PS, an endothermic peak at about 150 °C attributed to the crystalline starch melting was observed in all curves of the blends regardless of the WPU content. It demonstrated that the addition of WPU in the PS matrix does not change its crystalline type, which is in good agreement with the result from WAXD. In addition, no endothermic peaks, assigned to the melting of PCL (soft segment) crystalline, are observed in all curves, indicating the amorphous nature of the WPU. From Table 1, however, we can see the values of ΔH_m, namely the degree of crystallinity, decreases as the WPU was incorporated. Generally, the retrogradation of PS is greatly dependent on the hydrogen bond-forming abilities of the additives with starch molecules. The stronger the hydrogen bond between starch and the additives, the more difficult for starch to re-crystallize during the storage time of PS. The relatively lower values of ΔH_m of SU-10 and SU-20 indicated the stronger interactions and better compatibility. Furthermore, there is no occurrence of shoulder peak

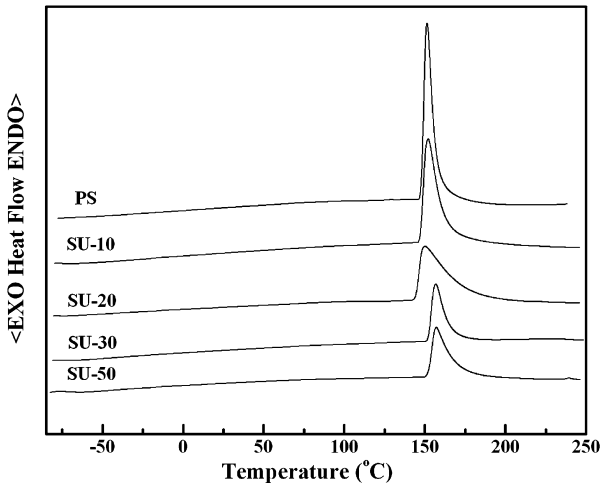

Fig. 3. DSC thermograms of PS and PS/WPU blends with different WPU contents.

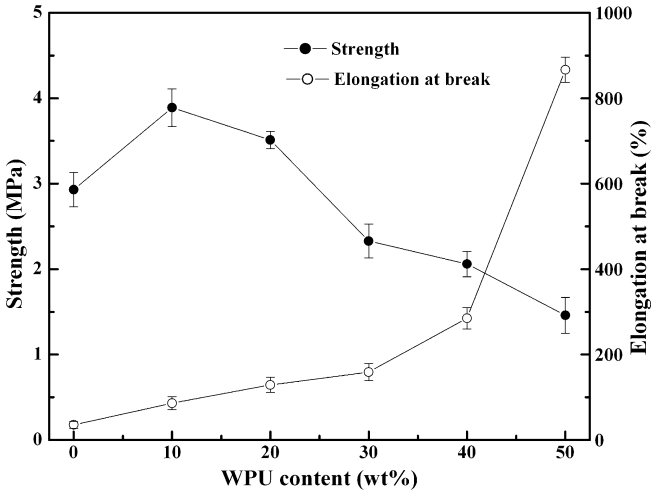

Fig. 4. The tensile strength and elongation at break as a function of WPU content for the PS and PS/WPU blends.

Table 1
The DSC data of PS and the PS/WPU blends

Sample	T_m (°C)	ΔH_m (J/g)
PS	152.5	24.78
SU-10	151.3	22.77
SU-20	149.3	21.71
SU-30	152.3	22.88
SU-40	156.4	24.33
SU-50	156.0	24.45

on the melt endotherm of all DSC curves, indicating no new crystallinity in this case. This is supported by WAXD results as well as. Generally, the PS plasticized by glycerol existed a complex heterogeneous system composed of glycerol-rich domains dispersed in a starch-rich continuous phase (Averous & Boquillon, 2004), and each phase should exhibit its own glass transition temperature (T_g) (Angles & Dufresne, 2000). Unfortunately, the T_g transitions were not detectable on the DSC curves in this case due to the low sensitivity of DSC (Heijkants et al., 2005a) and the very low heating capacity change (ΔC_p) of starch (Wu & Zhang, 2001).

3.3. Mechanical properties

Fig. 4 shows the effects of the WPU content on the tensile strength and elongation at break of the PS and PS/WPU blend films. The values of strength and elongation at break for the WPU film were 4.71 MPa and 1086% (data not shown), respectively. The tensile strength of the PS/WPU films firstly increased as the WPU was incorporated and reached a maximum value of 3.89 MPa for SU-10. The tensile strength of films was further decreased beyond SU-10. However, both SU-10 and SU-20 have a higher value than that of PS (2.93 MPa). This can be explained by the fact that the blends possess a good compatibility while the WPU content was lower than 20 wt%, and the phase separation occurred and became more severe when the WPU content ranged from 30 to 50 wt%. It is worth noting that the values of elongation at break of the blend films gradually increase from 35% to 886% with an increase of WPU content from 10% to 50%. It is contrary to the results of TPS/PCL blends reported by Averous et al. (Averous, Moro, Dole, & Fringant, 2000). The elongation of the TPS/PCL blends decreases significantly with an increase of PCL content. It can be ascribed to the difference of morphology of the PCL and the PCL based WPU, PCL is a semi-crystalline polymer, whereas the WPU is amorphous due to the interaction between the soft and hard segments (Ping et al., 2005). Especially, the significant increase of elongation at break of the SU-50 film can be easily observed. Therefore, the mechanical properties of the PS, both the tensile strength and elongation at break, can be improved by introduction of an appropriate content of WPU.

3.4. Water absorption

As one of the major drawbacks in the use of starch-based material is their water absorption tendency, any improvement in water resistance is highly important. The water uptake of the various PS/WPU blends versus time was evaluated. It was observed that each blend absorbed water during the experiment. The water uptake of the PS, WPU and PS/WPU films during conditioning in 98% RH as a function of time is shown in Fig. 5. It can be easily found that the PS is water sensitive and absorbs water very fast, while the WPU is basically waterproof and absorbs water very slowly although it is quite hydrophilic. In addition, two well-separated zones are displayed in all the curves for PS and PS/WPU blends. When $t < 48$ h, the kinetics of absorption is fast; whereas at extended time, $t > 48$ h, the kinetics of absorption becomes slow. Meanwhile, the water uptake after conditioning for 144 h in 98% RH versus the WPU content is plotted in Fig. 6.

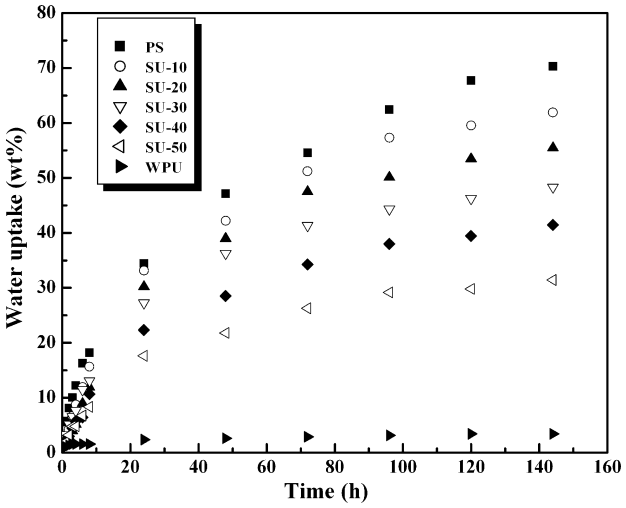

Fig. 5. Water uptake during conditioned at 98% RH versus time for the PS, WPU, and PS/WPU blends.

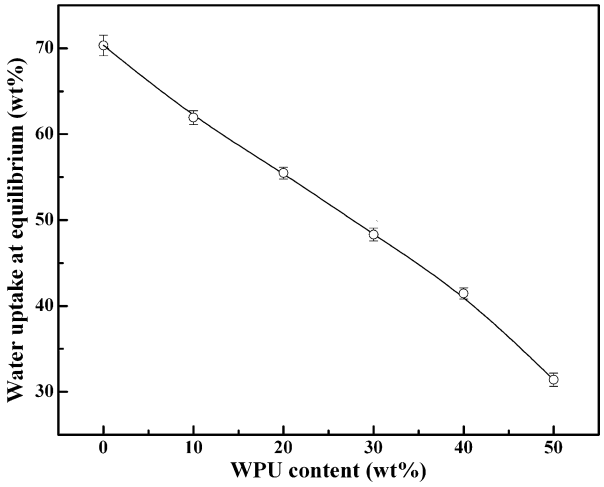

Fig. 6. Water uptake at 114 h and 98% RH for the PS and PS/WPU blends.

The water uptake of the PS film is around 70 wt%, while that of the SU-50 with 50 wt% content of WPU is only around 31 wt%. As we know, the diffusivity of water is strongly influenced by the microstructure of the material and the water affinity of the polymer components. Therefore, the decreased water uptake of the blends at the elevated WPU content can be explained by the fact that the swelling of the material is reduced in the presence of WPU within the PS matrix. Meanwhile, the relative low water-sensitivity of WPU and low glycerol content to whole material also might be responsible for the reduction of the water uptake.

4. Conclusions

Biodegradable blends were prepared from glycerol plasticized pea starch and PCL-based waterborne polyurethane. The blends showed good miscibility between the PS and the WPU when WPU content was lower than 20 wt%, due to the hydrogen bonding interactions between the carboxyl, carbonyl, urethane groups of WPU, and hydroxyl groups of starch. Introduction of the WPU significantly changed the properties of the PS. Compared with pure PS, the tensile strength of blends increased from 2.93 to 3.89 MPa by incorporation of 10 wt% WPU. It is worth noting that the elongation at break of PS/WPU blends increased significantly from 35% to 886% with WPU content ranging from 0 to 50 wt%. The presence of WPU also decreased the water uptake of the PS/WPU blends. This work provides a new and simple way to overcome the brittleness and moisture sensitivity for PS by blending biodegradable WPU. The resulting materials could have great potential applications.

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