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Structure and properties of urea-plasticized starch films with different urea contents

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ABSTRACT

Films of thermoplastic starch (TPS) plasticized with different contents of urea were prepared by using a solution casting method. Scanning electron microscopy, X-ray diffraction and IR spectroscopy were used to characterize structures of the TPS films, respectively. Water vapor sorption isotherms and tensile properties of the films were determined. TPS films showed more smooth and transparent in appearance and less B-type crystallinity than the starch film without urea. The effect of urea content on the structure and behavior of the TPS film could be divided in three stages: (1) below urea 10% where urea interacted with starch via H-bonding and the films showed an antiplasticization effect, (2) from urea 10% to 30% where an apparent plasticization effect appeared on the starch because of free urea molecules as the effective plasticizer, and (3) a macroscopic phase separation occurred due to supersaturation of urea when urea content was more than 30%.

1. Introduction

Nowadays, more and more attentions are paid to natural and biodegradable polymers as disposable products for environmental protection and sustainable development, and there is a growing interest in non-food applications of starch. Starch and modified starches are widely used as food packaging materials (Avella et al., 2005), coatings (Fringant, Rinaudo, Gontars, Montpellier, & Reims, 1998), and textile sizing agents (Mostafa & El-Sanabary, 1997), and so on. However, the application of starch films is restricted owing to the brittle nature (Imberty & Perez, 1988). The brittleness of starch materials is, among other things, mainly due to strong interactions between starch macromolecules (Takahashi, Kumano, & Nishikawa, 2004), which may confine the polymeric segmental mobility (Muscat, Adhikari, Adhikari, & Chaudhary, 2011). From polymer science point of view, polymeric segmental mobility can be improved by doping some hydrophilic plasticizers, as a result of having interactions between plasticizer–starch instead of between starch–starch. Mathew and Dufresne (2002) revealed that polyols are a group of efficient plasticizers for starch, for example, glycerol (Yu, Wang, Wu, & Zhu, 2008), xylitol (Liu, Chaudhary, Ingram, & John, 2011), sorbitol (Müller, Yamashita, & Laurindo, 2008), and short-chain glycols (Róz, Carvalho, Gandini, & Curvelo, 2006), as well as water. Another group of plasticizers for starch is amide-containing molecules, typical examples of which are formamide, acetamide and urea (Ma & Yu, 2004; Ma, Yu, & Feng, 2004). Thermoplastic starches (TPS) can be obtained by such conventional thermoplastic processing techniques as extrusion (Liu et al., 2011), compression molding (Róz et al., 2006) and injection molding (Gomes, Ribeiro, Malafaya, Reis, & Cunha, 2001), as well as the casting technique after starch mixtures are gelatinized (Mathew & Dufresne, 2002; Müller et al., 2008).

Plasticizers in TPS can restrain the retrogradation of starch and improve the mechanical properties of starch materials (Zullo & Iannace, 2009). Coating performance of starches can also be improved by plasticizers, along with a homogeneous, clear and smooth feature in appearance (Laohakunjit & Noomhorm, 2004). Mechanical properties of starch material depend on the polymer microstructure that was held together by starch–starch and starch–additive interactions via H-bonding, ionic bond and van der Waals forces (Avérous & Halley, 2009; Imberty & Perez, 1988). There are ordered crystallites in starch matrix and random chain entanglements in amorphous regions (Liu, Lv, Hu, Shan, & Zhu, 2010). A plasticizer not only can reduce the crystallinity, but also reduce the interaction between starch molecules in the amorphous region (Zhu, Li, Huang, Chen, & Li, 2013). In an appropriate range of the plasticizer content, a flexible starch material can be obtained. However, if the plasticizer content is too high, the TPS behaves like a gel or paste (van Soest & Vliegenthart, 1997). Therefore, TPS properties are directly influenced by plasticizer contents. There is a critical plasticizer content, below which the plasticizer molecules combine with starch polymer up to the saturation of bonding sites of starch

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molecules (Godbillot, Dole, Joly, Rogé, & Mathlouthi, 2006), and tensile strength and Young modulus increase, but elongation at break and water vapor absorption decrease with the increase of the plasticizer content (Yu et al., 2008). This is called "anti-plasticization effect" (Ayadi & Dole, 2011). As the plasticizer content is above the critical value, a real plasticization occurs, which shows rapid increases in elongation at break and water vapor absorption along with rapid decreases in tensile strength and modulus (Yu et al., 2008).

Although urea has been used for plasticization of hydrocellulose (Starunskaya, Tsygankov, Irklei, Bychkovskii, & Dobina, 1983), poly(vinyl alcohol) (Jiang et al., 2012) and soy protein (Mo & Sun, 2001), as well as starch (Ma & Yu, 2004; Ma et al., 2004; Maatoug, Ladhari, & Sakli, 2007), it is necessary to do intensive studies about effects of urea content on plasticized starch for industrial application. Urea has two amino groups and one carbonyl group with strong hydrophilicity and a tendency to crystallize, which is different from polyols. In the paper, we are attempting to reveal the structure and behavior of urea-plasticized starch films.

2. Materials and methods

2.1. Materials

A mild oxidized cornstarch with carboxyl content of 0.04% was generously provided by Sililun New Textile Co., Ltd. (Suining, China). Urea and salts with analytical grade were purchased from Kelong Chemical Reagent Co., Ltd. (Chengdu, China). The salts were used to prepare saturated aqueous solutions for film equilibration under varied relative humidity (RH) before film testing and determination. These were LiCl (RH 11%), $MgCl_2$ (RH 33%), K_2CO_3 (RH 44%), $CuCl_2$ (RH 68%), and NaCl (RH 75%) (Yu et al., 2008).

2.2. Film preparation

Films were prepared by solution casting method. The suspension concentration of the system was fixed to be 5% on the dry starch basis. In the suspensions urea contents were 0, 5, 10, 15, 20, 25, 30, 35 and 50% w/w, relative to the total dry basis, respectively. After gelatinized at 95 °C for 90 min, each 50 mL of the pastes was poured on a glass dish (210 mm × 150 mm) lined with a polyester film of the same size as the dish. After dried at room temperature, the film with thickness about 0.7 mm was removed from the plate and separated from the polyester film.

2.3. Scanning electron microscopy (SEM)

The cast film was sputtered with gold and observed by using a scanning electron microscope (Inspect F., FEI Co., Hillsboro, OR).

2.4. X-ray diffraction (XRD)

XRD data of starch film samples were measured with a D/max-IIIA X-ray diffractometer (Rigaku Company, Japan) by using a Cu Kα radiation source. The film sample was exposed to the X-ray beam (40 kV, 35 mA). The scanning region of the diffraction angle $2\theta = 5–30^\circ$ with the scanning rate 0.03°/s. Samples were conditioned for one week in a desiccator with controlled RH 68% (over a saturated solution of $CuCl_2$) at room temperature prior to the measurement.

2.5. Infrared spectrum (IR)

The film samples were stored at room temperature and RH 68% for one week. IR spectra of the samples were recorded by attenuated total reflection (ATR) method on a FTS3000 FTIR Spectrum Scanner (Hercules, USA), over 32 consecutive scans with a resolution of 4 cm^{-1} at room temperature. Each film was allowed to contact tightly with the ATR crystal surface, and the free surface, i.e. the film surface contacting with the air in the film-forming process, was measured.

2.6. Water vapor sorption (WVS)

Starch films were equilibrated at temperature 20 ± 1 °C for 7 days at a series of RHs fixed by several separate saturated salt solutions. After equilibration, the precise weight of each sample (marked as W_1) was obtained. Then the conditioned sample was dried at 105 °C for 4 h, the weight of which was taken as W_2. The percentage of WVS was calculated as $(W_1 - W_2)/(W_2) \times 100\%$. Each test was done in triplicate.

2.7. Mechanical properties

The starch film was cut in strips (10 mm × 200 mm) and conditioned at 68% RH for one week. The exact thickness of the strips was measured over 10 points with a CH-10-AT centesimal thickness testing instrument (Shanghai Liuling Instrument Co., Ltd., China), and the average thickness of each sample was calculated. The mechanical property was determined by utilizing YG061 tensile testing equipment (Laizhou Electron Instrument Co., Ltd., China). The film strip was clamped between two grips with an initial clamping distance of 100 mm, and a stretching speed was set to 100 mm/min. For each sample, 10 replications were tested, and the average value was taken.

3. Results and discussion

3.1. SEM observation

As judged by SEM observation, the starch film without urea, Fig. 1(A), exhibited a rough surface. This is believed to be resulted from cocrystallization between amylose and amylopectin during the film formation at room temperature (Liu et al., 2010; Rindlav-Westling, Stading, & Gatenholm, 2002). By contrast, appearance of urea-plasticized oxidized cornstarch films with urea concentration 10% and 20% tended to be more even, smooth and transparent, as showed in Fig. 1(B) and (C). When the urea content was 35%, Fig. 1(D) showed some irregular educts appeared on the surface of the film.

3.2. Relative crystallinity

An Origin graphing and data analysis software (OriginLab, Northampton, USA) was used to show XRD patterns of starch films containing urea contents of 0%, 20% and 40%, and then to smooth the XRD curves by adjacent-averaging 20 points at extrapolated boundary condition, as Fig. 2 presented. The $2\theta = 16.9^\circ$ is a characteristic peak of the B-type crystal of starch relative to the {1 2 1} crystal face (Lopez-Rubio, Flanagan, Gilbert, & Gidley, 2008). MDI Jade 5.0 software (California, USA) was employed to calculate the relative crystallinity (RC) and the crystallite size (CS) at $2\theta = 16.9^\circ$ peak. For starch film samples containing urea 0%, 20% and 40%, the RC was 1.13%, 0.79% and 0.05%, respectively, corresponding to the CS 0.16 nm, 0.20 nm and 0.24 nm. This, along with the SEM photos for film samples, means that urea molecules can impede the B-type crystallization of the starch. In addition, a new peak at $2\theta = 22.4^\circ$ appeared on the curve of the film with urea 40%, which may be caused by separation of urea from starch matrix as shown in an inset on the right side of Fig. 2, and may explain the educts occurred on the film surface with urea content 35%.

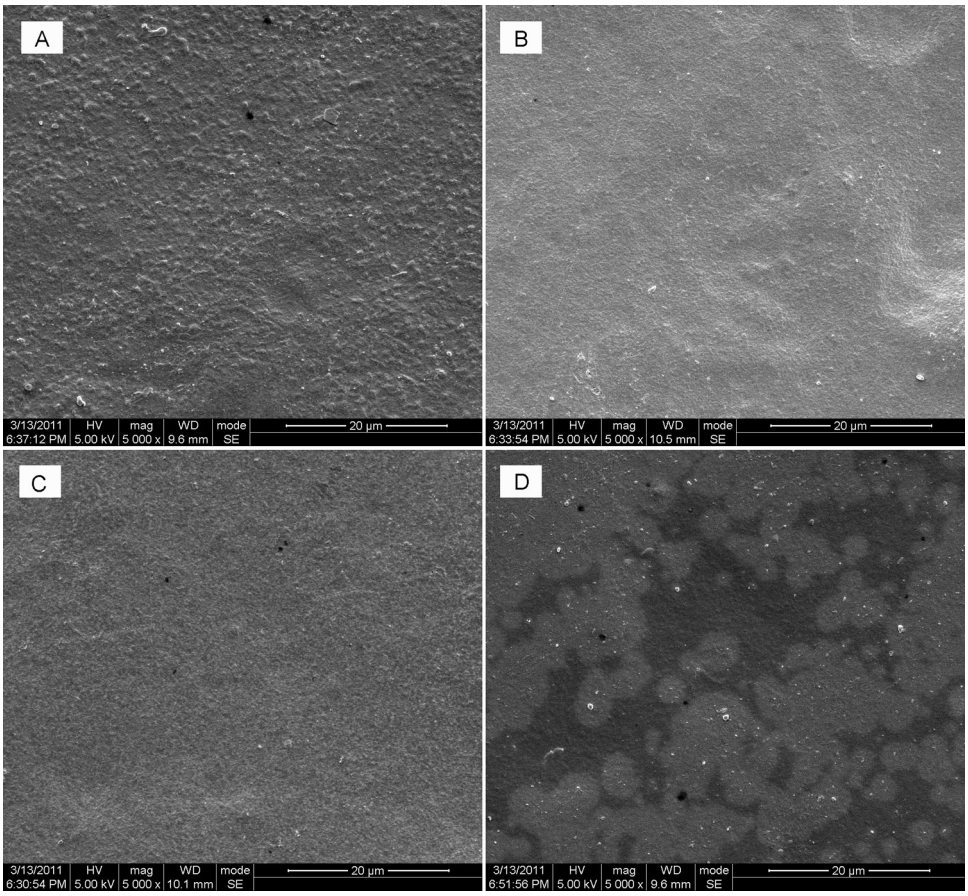

Fig. 1. SEM images of (A) oxidized cornstarch film and plasticized starch films with urea contents of (B) 10%, (C) 20% and (D) 35%, respectively, based on total dry weight.

3.3. FTIR–ATR spectroscopy

It is meaningful to show some chemical components of a solid surface especially for a polymer composite, for which FTIR–ATR spectroscopy is one of the most appropriate analytic methods (Ferreira et al., 2009). Fig. 3(a) showed the spectra of plasticized oxidized cornstarch films with various urea contents. It was shown from Fig. 3(b) that three absorption bands appeared at about 3449, 3339 and 3208 cm^{-1} in the high wavenumber region once urea had been added. Two peaks of 3449 and 3339 cm^{-1} were from the red shift of 3442 and 3344 cm^{-1}, respectively, associated with H-bonding formation of N—H in urea (Ceraulo, Dormond, Mele, & Liveri, 2003). This means the interaction between urea and starch. In addition, the 3208 cm^{-1} band could stem from the frequency of 3258 cm^{-1} corresponding to the O—H stretching vibration of starch (Kizil, Irudayaraj, & Seetharaman, 2002; Santha, Sudha, Vijayakumari, Nayar, & Moorthy, 1990). The red shift to a lower frequency of about 50 cm^{-1} suggested a stronger strength of H-bonding interaction between O—H of starch and N—H of urea than that between the —OH pairs in starch.

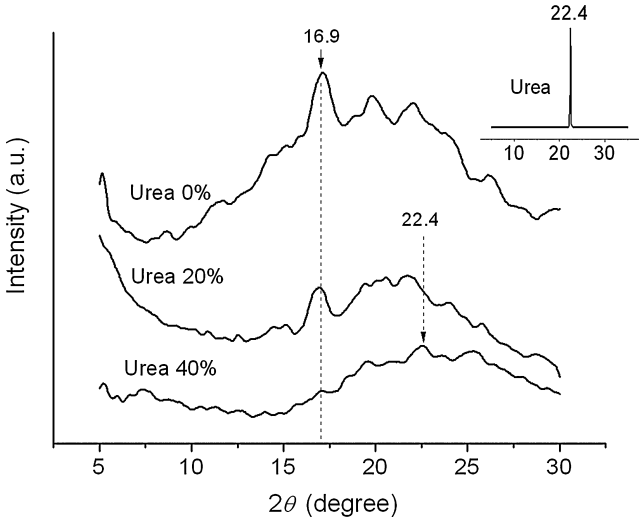

Fig. 2. X-Ray diffractograms of oxidized cornstarch films with urea contents of 0%, 20% and 40%.

Evidence of H-bonds formed between starch and urea in the TPS could also be observed in Fig. 3(c) for IR spectra in the wavenumber range of 1000–900 cm^{-1}. At 989.5 cm^{-1} absorbing peak for the starch film (urea 0%) due to C—O—H bending vibrations (Capron, Robert, Colonna, Brogly, & Planchot, 2007; Kizil et al., 2002), a blue shift was observed to 991.4 cm^{-1} for starch–urea TPS. In addition, the infrared band at about 927.8 cm^{-1} is attributed to the skeleton mode vibrations of α-1,4-glycosidic linkages (C—O—C) in the starch (Tatongjai & Lumdubwong, 2010). The band changed to 929.7 cm^{-1} for the films of urea 5% and successively to 931.6 cm^{-1} (urea 10%), and the change stopped at 933.5 cm^{-1} (urea 15% or more). It suggests that the C—O—C linkages in the starch also gradually engaged the formation of H-bonds in the starch–urea system with an increase of urea.

In Fig. 3(a) three characteristic peaks of urea appeared, 1659, 1626 and 1453 cm^{-1}, as urea was added in. The 1659 cm^{-1} band is originated from C=O stretching (amide-I region), 1626 cm^{-1} from N—H bending (amide-II region), and 1453 cm^{-1} from C—N stretching (Ceraulo et al., 2003). No changes in frequency were

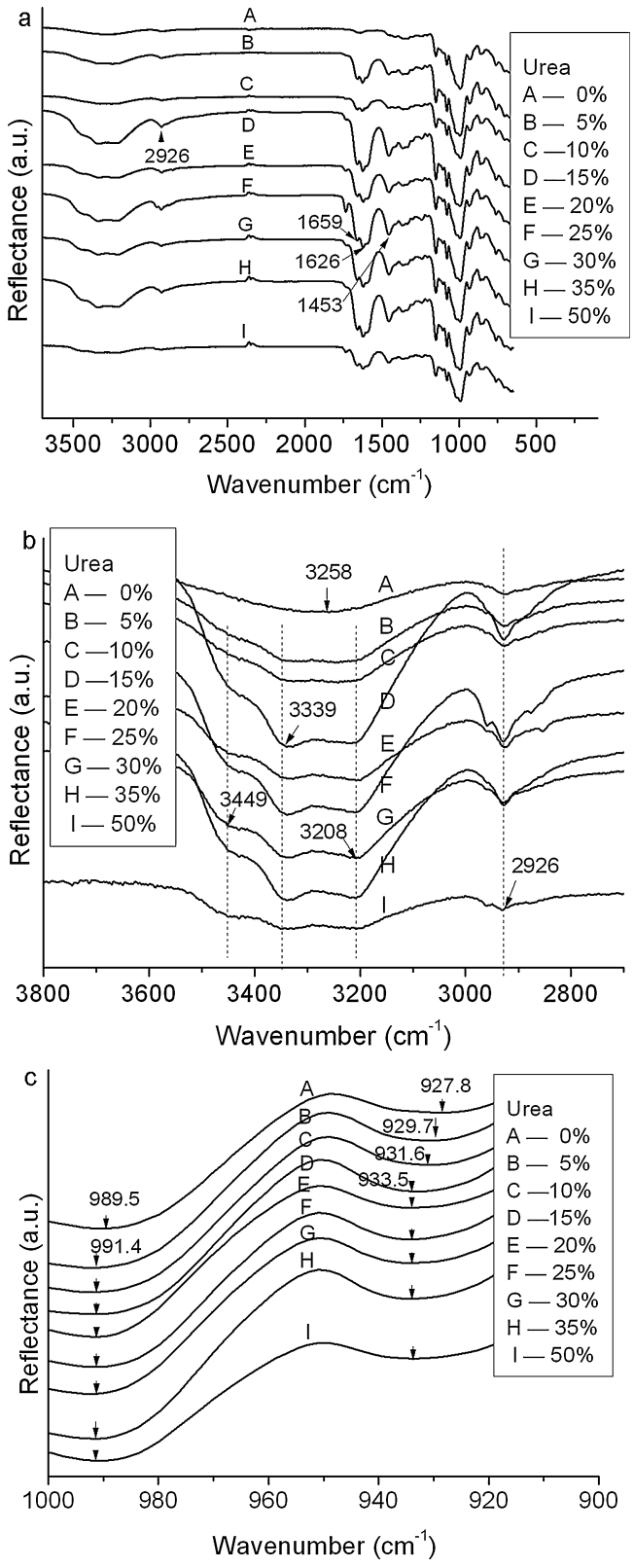

Fig. 3. FTIR–ATR spectra of plasticized starch films with varied urea content in frequency ranges of (a) 3750–500 cm^{-1}, (b) 4000–2800 cm^{-1} and (c) 1000–900 cm^{-1}.

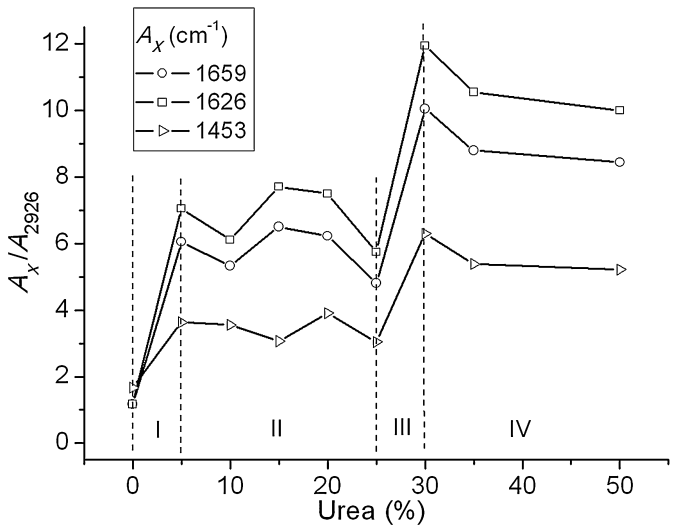

Fig. 4. The ratio of H_x/H_{2926} as a function of urea content.

observed for these peaks, but the absorption intensity at these frequencies varied with urea contents. In order to know the variation, we replaced reflectance values in the figure with absorbance values, and took the absorbance band 2926 cm^{-1}, assigned to $\rangle CH_2$ stretching in starch pyranose ring (Kizil et al., 2002) as a reference value, named as A_{2926}. In the same spectrum for a film sample, the ratios of absorbance values at 1659, 1626 and 1453 cm^{-1} to A_{2926} were calculated as A_x/A_{2926}, respectively, where x represented 1659, 1626 or 1453 cm^{-1}. Changes of the ratio A_x/A_{2926} with urea content were shown in Fig. 4.

From Fig. 4, we know that the three curves, relative to 1659, 1626 and 1453 cm^{-1}, had a similar variation trend. The A_x/A_{2926} values had a sharp increase from 0% to 5% urea contents (named as region I), then were in a relatively fluctuating plateau with urea content 5–25% (region II), followed by another sharp increase of the A_x/A_{2926} in urea 25–30% (region III) and another plateau in urea content of 30–50% (region IV). In view of that the IR beam in ATR mode can only pass through the top surface of the film measured, the average penetration depth in the sample is about 2 μm in the wavenumber range 1065–870 cm^{-1} (Capron et al., 2007). The variation of the A_x/A_{2926}, therefore, represented the changes of surface concentration of urea on the starch film.

In the region II, the first fluctuating plateau of A_x/A_{2926} indicated small changes of urea absorption strength on the film surface. This implied that urea could be moderately interacting via H-bonding with starch in the matrix. As showed in Fig. 3(c), C—O—C band vibration of the starch was blue-shifting from 927.8 cm^{-1} to 933.5 cm^{-1} until urea up to 15%, which could be, more or less, relative to the course of saturation of the H-bonding site. Another higher fluctuating plateau in region IV in Fig. 4 could involve in supersaturation of urea (Yu et al., 2008). This interesting phenomenon suggested that urea molecules could interact with starch till the content up to about 25–30%, above which the urea tended to move to the film surface. This, together with the film appearance of SEM photos, showed a macroscopic phase separation occurred as the urea content equaled or more than 30%.

3.4. Water vapor sorption isotherms

WVS isotherms of the TPS with different urea contents at various RHs are shown in Fig. 5. At certain urea contents, WVS values increased with increasing RH. While at a constant RH, WVS decreased firstly to a turning point and then began to increase with increasing the urea content. With the aid of some auxiliary lines,

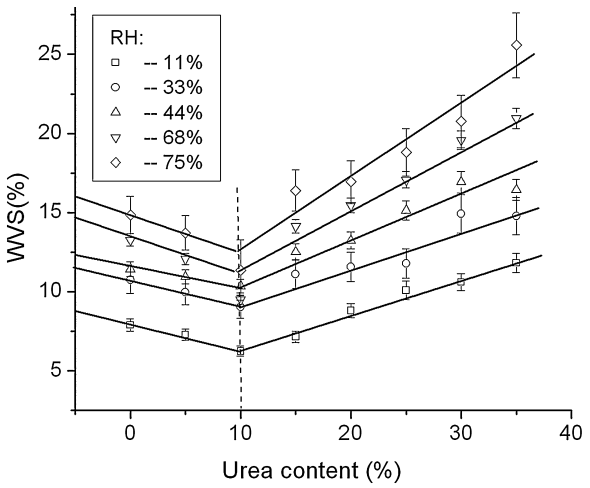

Fig. 5. Water vapor sorption isotherms as a function of urea content at varied RH.

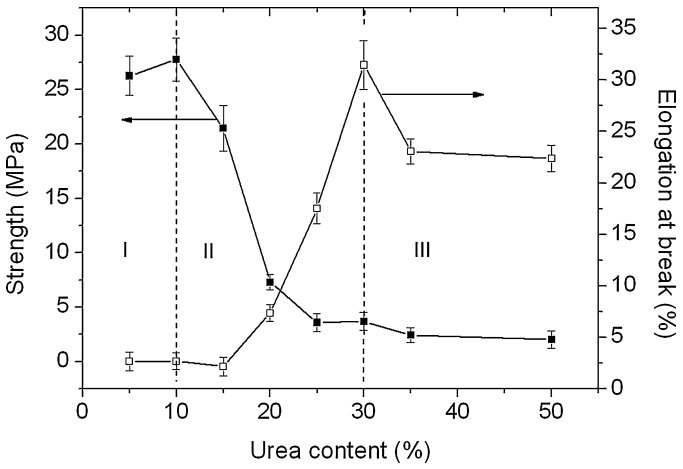

Fig. 6. Tensile properties of plasticized starch films with various urea contents.

we could see two regions separated by a dividing line that linked turning points of all the curves, and the dividing line passed through the abscissa at urea content 10%. On the left side of the dividing line in all the RH conditions, WVS decreased as urea content increased. This phenomenon has been ascribed to a typical antiplasticization effect, as a result of interaction between a glassy polymer and a plasticizer at the molecular level (Godbillot et al., 2006; Lourdin, Bizot, & Colonna, 1997). The antiplasticization effect can decrease local macromolecular mobility that correlates with a decrease in β-transition temperature of plasticized starches (Gaudin, Lourdin, Forssell, & Colonna, 2000). Godbillot et al. (2006) ascribed the turning point to the H-bonding saturation of polymer sites with plasticizers. Below these points at various RHs in our discussions, urea molecules interacted with starch via H-bonding, which partly concealed hydrophilic sites of starch, and thus decreased the WVS value.

In the H-bonding process water will also take part in competing with plasticizer (Godbillot et al., 2006). The dividing line in Fig. 5 was almost parallel to the WVS axis, independent of the RH variation. This means less contribution of water vapor to the saturation of the H-bonding sites in starch. In other words, urea reacted with starch via H-bonding prior to water as urea content was less than 10% in the starch matrix. The rationale is based on the electronegativity between pairs of acceptor and donor involving H-bonding. If starch is the acceptor of the hydrogen, where C—O—C glycosidic linkage and C—O in a hydroxyl group in starch will play the parts, the hydrogen-donating effect of amide group in urea will be higher than the hydroxyl of water. On the contrary, for the donor of the hydrogen is the hydroxyl group of starch, the electronegativity of nitrogen in urea is lower than the oxygen of water. In the competition of the H-bonding with starch, therefore, water is always weaker than urea. The same thing holds true when it comes to plasticization effect between urea and glycerol on starch. Ma and Yu (2004) claimed that the H-bonding ability of urea is greater than glycerol on the basis of comparing the FTIR spectrum of urea-TPS with that of glycerol-TPS.

On the right side of the dividing line, WVS values increased with urea contents. This phenomenon could involve water uptake by free plasticizer molecules with the intrinsic hydration of urea, by hydrophilic groups of starch and their combination (Godbillot et al., 2006) in the urea–starch TPS.

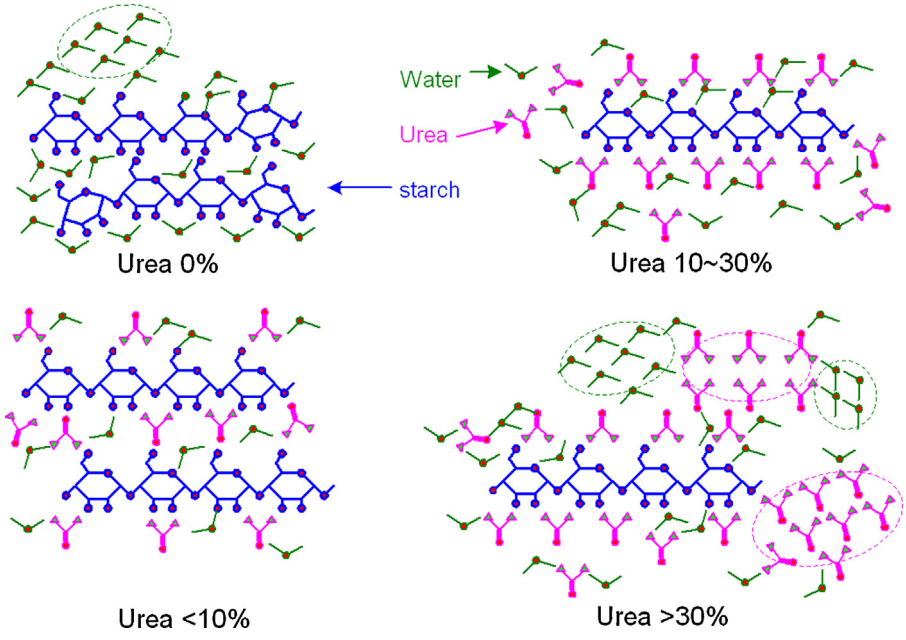

Fig. 7. Schematic representation of urea states in urea-plasticized TPS with different urea concentrations.

It seems clear from Fig. 5 that urea molecules at low contents (below about 10%) linked to starch via H-bonding until the saturation point of the starch-binding site. As urea contents were more than 10%, urea molecules exceeded the saturation point of H-bonding site of starch, and then had a tendency to combine with water or to be clustered by self-aggregation. So that WVS depended on both urea content and RH.

3.5. Mechanical properties

As showed in Fig. 6, tensile strength (TS) and elongation at break (*E*%) of the urea-plasticized TPS varied with urea content. The urea-free film (the control sample) was too brittle to be tested, so no data for the control sample were in the figure.

The tensile properties could be discussed in association with antiplasticization (Godbillot et al., 2006) and plasticization effects (Lourdin et al., 1997) in three steps (Yu et al., 2008). The first step is that the TS of the samples slightly increased with increasing urea content till 10%; meanwhile, the *E*% of the starch films reached the bottom value as urea content was about 10%. This step showed a typical antiplasticization effect and well matched the decrease of WVS occurred on the left side of Fig. 5. And in this step, the interaction of urea and starch dominated owing to the stronger H-bonding between amino of urea and hydroxyl of starch than that between hydroxyl pair of water and starch (Ma & Yu, 2004; Ma et al., 2004), which resulted in less water uptake in the starch matrix. In the second step in urea range of 10–30% there were a rapid decline of TS and a fast growth of the *E*% with a typical plasticization effect. In the last step corresponding to urea content above 30%, the TS kept the lowest values, but the *E*% reduced firstly and then unchanged with further increase of urea. This could result from macroscopic phase separation, relevant to supersaturation of urea in the system.

4. Conclusions

A mild oxidized cornstarch was mixed with various contents of urea, gelatinized and cast into films. The structure and properties of the urea-plasticized TPS were controlled by the urea content. Based on the experimental results a schematic representation was proposed for urea states in starch as Fig. 7 showed, and conclusions can be drawn as follows:

As urea content was 10% or less, urea was caught by starch polymer mainly through H-bonding in replacement of that between water–starch and inter- and intra-molecular interactions of starch. This could obstruct B-type crystallization as well as mobility of starch segments. A typical antiplasticization occurred owing to less water absorption, and the performances changed, such as enhanced tensile strength and reduced elongation at break with increasing urea content.

As urea content was more than 10%, urea molecule began to be free from starch catching because of no more active H-bonding sites on the starch. Free urea acted as an effective plasticizer and moisture absorbent. Both free urea and enhanced water vapor sorption facilitated the motion of starch segments. As a consequence, with the increase of urea content the tensile strength of the TPS decreased, and the elongation at break increased.

When urea content was at 30% or above, a macroscopic phase separation of the TPS film occurred owing to supersaturation of urea in the starch matrix. That was not in favor of the appearance and tensile properties of the TPS film.

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