Effect of urea and formamide plasticizers on starch/PVA bioblend sheets

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ABSTRACT: The starch/polyvinyl alcohol (PVA) bioblend sheets containing urea and formamide as plasticizers were prepared through melt processing in presence of water. The experiments indicated that urea and formamide plasticizers could form strong hydrogen bonds with starch/PVA molecules. Urea exhibited better plasticizing effect than formamide. Urea also could greatly destroy the crystal structures of PVA component in the blends, leading to the decreased crystallinity of the blends. Formamide was a good solvent for urea and could prevent urea separating from the blends, resulting in the improved stability of plasticizing systems. The blends exhibited good flexibility. Therefore, the incorporation of both urea and formamide into starch/PVA blends could exhibit synergistic effects to ensure the blends with both good plasticizing effect and the stability of the plasticizing systems. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42311.

INTRODUCTION

Biodegradable plastics that can be easily degraded in the natural environment are arousing the public interest since the petroleum-derived plastics had caused worldwide problems of environment pollution and resources crisis.[1,2] Products derived from the agricultural resources—for example, starch, protein, cellulose, etc.—provide a good substitute resource to develop the biodegradable materials.[3–5] Starch is increasingly used for various purposes due to its low cost and abundant availability.[6–8] However, the entire starch-based products lack strength and rigidity, which limit their applications in material engineering.[9] In order to compensate the poor property of entire starch products, blends of starch with polyvinyl alcohol (PVA) have been used as potential biodegradable polymers to replace the entire starch plastics.[10] PVA is a kind of petroleum-based biodegradable polymer, and possesses excellent chemical resistance, optical and physical properties, good film-forming capability, water solubility, and excellent biocompatibility.[11,12] The strength, flexibility, and water resistance of starch products could be improved with PVA incorporation.[13] Plasticizers, such as glycerol,[14] polyethylene glycol,[15] urea,[16] ascorbic acid,[17] sorbitol,[18] citric acid,[19] tartaric acid,[20] and calcium chloride,[21] were usually incorporated to improve the flexibility of the blends. Usually, starch/PVA blends are prepared by solution casting.

However, this method has many drawbacks such as low solution density, low production, high energy consumption, and so on, which restrict their applications.

Another way to prepare starch/PVA blends is melt processing, which is more efficient for large-scale production. However, the thermal processing of starch is difficult without plasticizers due to the poor flowability. Therefore, plasticizers with high plasticizing efficiency would be indispensable. During the preparation, plasticizers form hydrogen bonds with starch, and transform them thermoplastic.[22]

In this study, the mixture of urea and formamide, which has been proved good plasticizing effect on starch[23] and PVA,[24] was used to prepare starch/PVA blend sheets. The effect of urea/formamide plasticizers on the structure and properties of starch/PVA bioblends through melt processing was investigated. We aim to provide an economic way to prepare biodegradable starch/PVA bioblend sheets with excellent properties. It is expected that these blend sheets have potential applications in disposable packaging areas.

MATERIALS AND METHODS

Materials
PVA (117) with the viscosity of $25.0–31.0 \times 10^{-3}$ Pa·S and alcoholysis degree of 98.0–99.0 mol/% was purchased from

Table I. Composition and Codification of Starch/PVA Blends

Sample	PVA	Starch	Water	Urea	Formamide
U10F0	50	50	50	30	0
U7F3	50	50	50	21	9
U5F5	50	50	50	15	15
U3F7	50	50	50	9	21
U0F10	50	50	50	0	30
W-starch	0	100	80	0	0
W-PVA	100	0	80	0	0
W-starch/PVA	50	50	80	0	0

Kuraray Co., Ltd. (Japan). Corn starch was purchased from Quanfeng Co., Ltd. (Beijing). Formamide and urea were supplied by Sinopharm Chemical Reagent Co., Ltd (Beijing, China) and used as received.

Preparation of Starch/PVA Bioblends

Starch, PVA, water, and plasticizers (formamide and urea) in different weight ratios were mixed in a high-speed mixer (GH-10, Zedao Mechanical Technology, Beijing, China) at room temperature for 3 min. The ratio of starch and PVA was fixed at 1 : 1. The content of the plasticizers and water was fixed at 30 and 50 phr based on the solid materials (starch and PVA, respectively). Then the mixtures were charged into a HAAKE torque rheometer (TA Instruments, USA) and further mixed at 105°C for 10 min with a stirrer speed of 80 rpm. For the rheomoeter is not as airproof as extruder, water is easy to evaporate at high temperature. Therefore, the torque data was not discussed in this study. The mixtures were compression molded on plate vulcanizing machine (XLB-400, Huaqing Industry Group, Qingdao, China) to obtain the bioblend sheets with thickness of about 0.5–0.6 mm. The molding temperature, pressure, and time were 110°C, 20 MPa, and 10 min, respectively. Composition and codification of the starch/PVA blends are listed in Table I. Three control samples (W-starch, W-PVA, and W-starch/PVA) were also prepared with only water added to facilitate the processing, and no urea or formamide plasticizers were incorporated. Before testing, all samples were vacuum-dried at 80°C for 2 days and kept at a relative humidity (RH) of 0% (conditioned by phosphorus pentoxide P_2O_5) for 2 weeks.

Characterization

Fourier-Transform Infrared Spectroscopy (FT-IR). The Fourier-transform infrared spectra of samples were recorded on a Nicolet 5700 FTIR spectrometer (Thermo Electron Corporation, Waltham, MA, USA). Samples were prepared by mixing the fine powder with potassium bromide (KBr) and pressing. The spectra were obtained at a resolution of 4 cm^{-1} in the range of 4000–400 cm^{-1}.

X-ray Diffraction (XRD). X-ray diffractograms were recorded using a DIP 2030 apparatus (MAC Science, Yokohama, Japan) using Cu–Kα radiation (15.4 nm) at 2θ values ranging from 5° to 40° at a scanning rate of 2°/min. The testing conditions were 40 kV and 30mA.

Differential Scanning Calorimeter (DSC). Differential scanning calorimetry was carried out using a DSC Q100 calorimeter (TA Instruments, USA) under a nitrogen atmosphere. An empty pan was used as reference. Samples were placed in an aluminum pan and were first heated from −70 to 235°C at a heating rate of 20°C/min and held for 3 min. Subsequently, a cooling scan was conducted from 235 to −75°C at 20°C/min cooling rate. The initial sample weight was in the range of 5–10 mg.

Scanning Electron Microscope (SEM). Scanning electron microscopy images were obtained on an SEM (VEGA II, TESCAN, S.R.O, Czech Republic). Samples in the dry state were frozen in liquid nitrogen, snapped immediately, and then vacuum-dried. The fractured surfaces (cross-sections) of the blend sheets were sputtered with gold before the SEM observation.

Moisture Uptake. The kinetics of water absorption at room temperature (25°C) was studied for all blends. The samples used were thin rectangular strips with dimension of 50 × 10 × 0.6 mm. The samples were vacuum-dried at 80°C for 2 days and kept at 0% RH (conditioned by P_2O_5) for 2 weeks. After weighing, the samples were conditioned in a desiccator containing NaBr saturated solution to ensure an RH of 58%. The samples were removed at specific intervals and weighed. The water uptake (WU) was calculated by

$$\text{WU (\%)} = \frac{m_t - m_0}{m_0} \times 100 \qquad (1)$$

where m_0 and m_t are the weights of the samples before and after a time t of conditioning, respectively.

Mechanical Testing. Specimens, with the shape of a dumb-bell according to the ASTM D638 standard, were prepared. Tensile tests were performed on a universal tensile testing machine (CMT 6104, SKYan, Shenzhen, China) equipped with 100 N load cell and operated at a cross-head speed of 50 mm/min. Five samples of each product were tested at room temperature and the average value was reported. Before testing, all specimens were conditioned at room temperature in a desiccator of 58% RH (conditioned by NaBr-saturated solution) for 2 weeks.

Thermogravimetric Analysis (TGA). Thermogravimetric analysis was performed on a TGA Q5000 thermogravimetric analyzer (TA Instruments, USA) from 50 to 800°C at heating rates of 10°C/min under nitrogen atmosphere. The sample weight was about 5–10 mg.

RESULTS AND DISCUSSION

FTIR Analysis

FTIR spectra of starch/PVA blends are shown in Figure 1(a). The peak at around 3300 cm^{-1} was assigned to the stretching vibration of ─OH groups. The peak shifted to lower wavenumbers with the addition of urea and formamide compared with W-starch/PVA blend (without urea and formamide plasticizers). The possible reason is that the ─C═O and ─NH$_2$ groups in urea or formamide could form new and stable hydrogen bonds with ─OH groups on PVA and starch molecules. As shown in Figure 1(b), the wavenumbers of ─OH stretching vibration peak gradually decreased and "red shift" was more obvious with the increase of urea, indicating stronger hydrogen bond between plasticizers and starch/PVA molecules. Urea could form
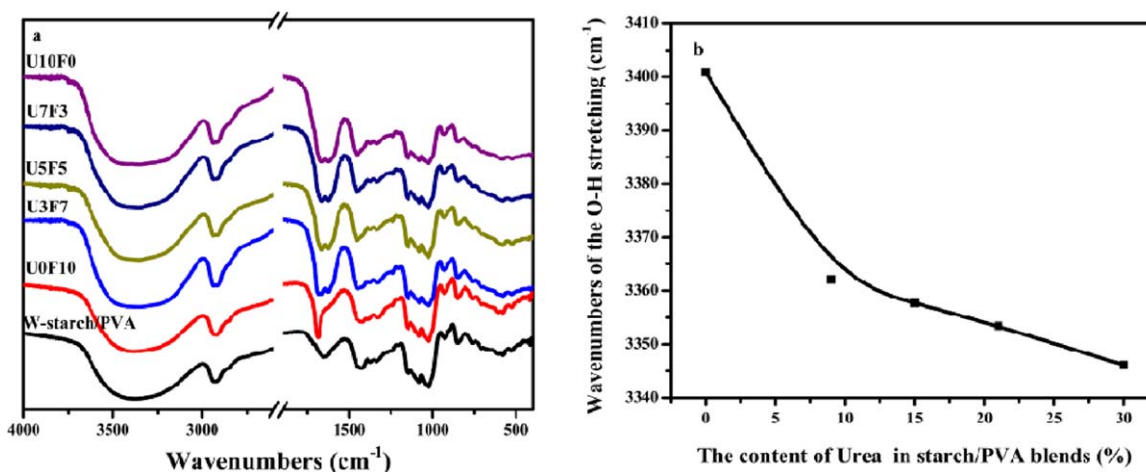
Figure 1. (a) The FTIR spectra of starch/PVA blends and (b) wavenumbers of the O—H stretching of the blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrogen bonds more easily with starch/PVA molecules than formamide, leading to a better plasticizing effect. The reason may be that the electronegativity of —C═O group in urea was higher than that in formamide. A new peak at around 1650–1700 cm^{-1} occurred after adding urea or formamide. It was resulted from the C═O group in urea and formamide. The wavenumber of the peak shifted from 1686 to1670 cm^{-1} with the increase of urea. It was also ascribed to the hydrogen bond between plasticizers and starch/PVA molecules.

XRD Analysis

XRD curves of starch/PVA blends are shown in Figure 2. The W-starch exhibited amorphous patterns. W-PVA showed an obvious diffraction peak at 19.8° corresponding to the (101) crystal plane of PVA. For the W-starch/PVA, most of the diffraction peaks were similar to those of W-PVA other than W-

starch, indicating that PVA and starch components dominated crystal zone and amorphous zone, respectively.

For the blends with urea and formamide plasticizers, the peak at around 19.8° was caused by the crystal structure of the PVA component. The intensity of crystal peak evidently decreased with the addition of urea and formamide. Urea and formamide could penetrate into crystallization zone of starch/PVA blends during the process above 100°C in the presence of water, and form new hydrogen bonds with starch and PVA molecules,[25] which destroyed the crystal structure of PVA in the blends. The degree of crystallization of the blends gradually decreased from 32.6 to 10.8% with the increase of urea as indicated in Table II, which demonstrated that urea could more likely destroy crystal structure of the blends than formamide.

It was worth noting that a new peak at around 22.5° appeared on the pattern of U10F0, which may be ascribed to the urea crystallization. The peak was not found for other blends. To further explore the reason for the peak, micrographs of the surface of U7F3 and U10F0 blend were recorded using BX-51 Polarizing microscope (Olympus, Japan). As shown in Figure 3, the micrograph of the surface of U10F0 blend revealed a lot of strip structures, indicating that urea might have separated from the blend. The phenomenon was not found on the surface of U7F3 blend. The reason may be that formamide was a good solvent for urea, and could resist urea separating from the blends. For plasticizers, urea could sharply destroy crystal structures of the
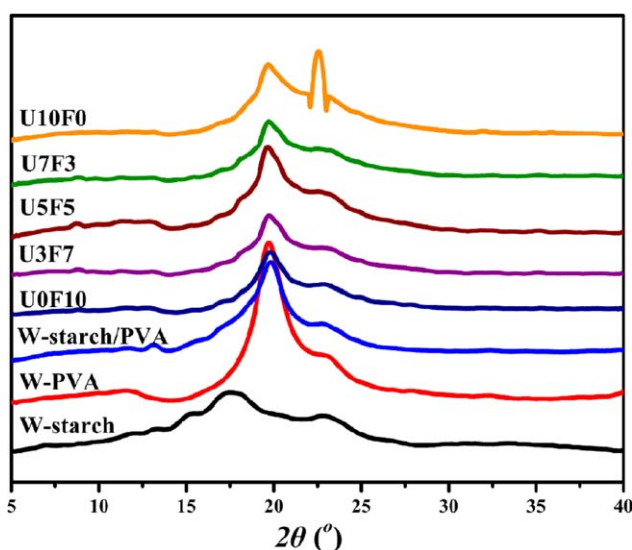

Figure 2. The XRD curves of W-starch, W-PVA, W-starch/PVA, and starch/PVA blends containing urea and formamide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Crystallinity Starch/PVA Blends from XRD Characterization

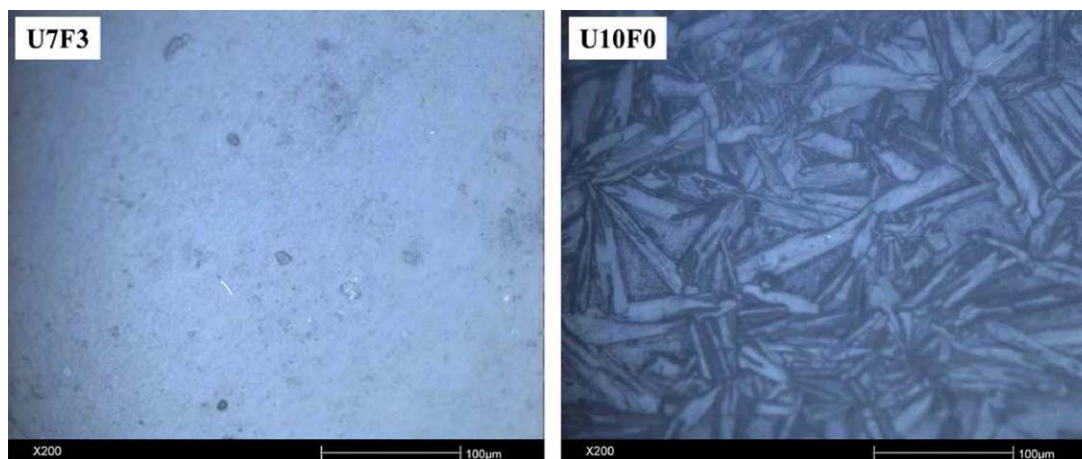| Sample	Crystallinity (%)
W-starch/PVA	32.6
U0F10	23.3
U3F7	20.1
U5F5	17.5
U7F3	16.1
U10F0	10.8

Figure 3. Micrographs of the surface of U7F3 and U10F0 blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]
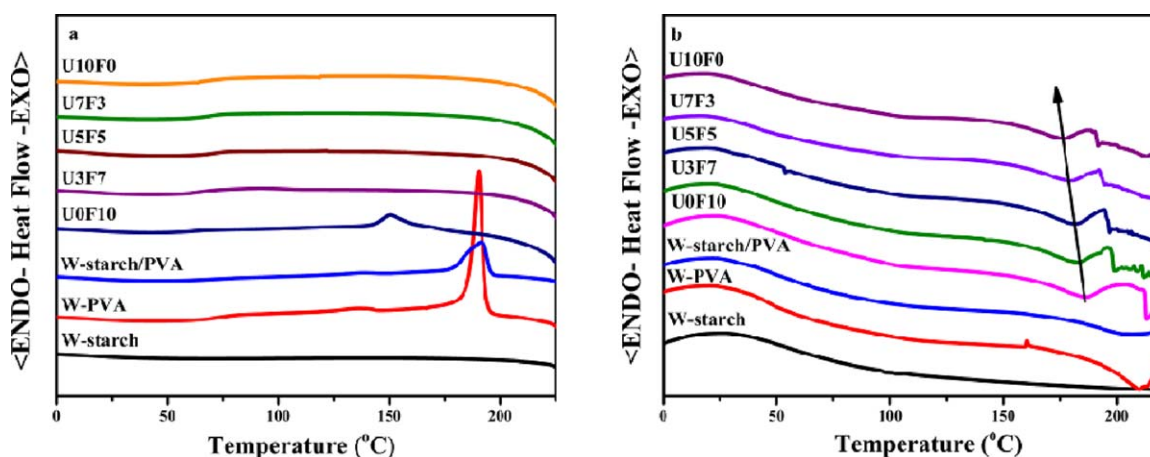

Figure 4. The (a) exothermic curves and (b) endothermic curves of W-starch, W-PVA, W-starch/PVA, and starch/PVA blends containing urea and formamide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

blends. Formamide played an indispensable role, which could ensure the stability of the plasticizing systems. The incorporation of both urea and formamide into starch/PVA blends could exhibit synergistic effects to ensure the blends with both good plasticizing effect and the stability of the plasticizing systems.

DSC Analysis

The exothermic curves of W-starch, W-PVA, W-starch/PVA, and starch/PVA blends containing urea and formamide are shown in Figure 4(a), and the relating parameters are listed in Table III. No crystallization peak was observed on the exothermal curve of W-starch, indicating its amorphous structure. A sharp peak was observed in the exothermal curve of W-PVA, which was assigned to the crystallization of PVA. For W-starch/PVA blend, a broad peak at 191.5°C was observed, that was resulted by the PVA crystallization. The T_c (crystallization temperature) of U0F10 at 150.8°C was lower than that of W-starch/PVA blend due to the plasticizing effect of formamide. However, the crystallization peak of the blends was not observed when urea was added, indicating that urea could greatly destroy the crystal

structures of the blends, which was in conformity with the XRD results.

The endothermic curves of starch/PVA blends containing urea and formamide are shown in Figure 4(b). No melting peaks were observed in the exothermal curve of W-starch. A sharp melting peak at 210.0°C was observed in W-PVA, indicating its

Table III. Results from the DSC Tests

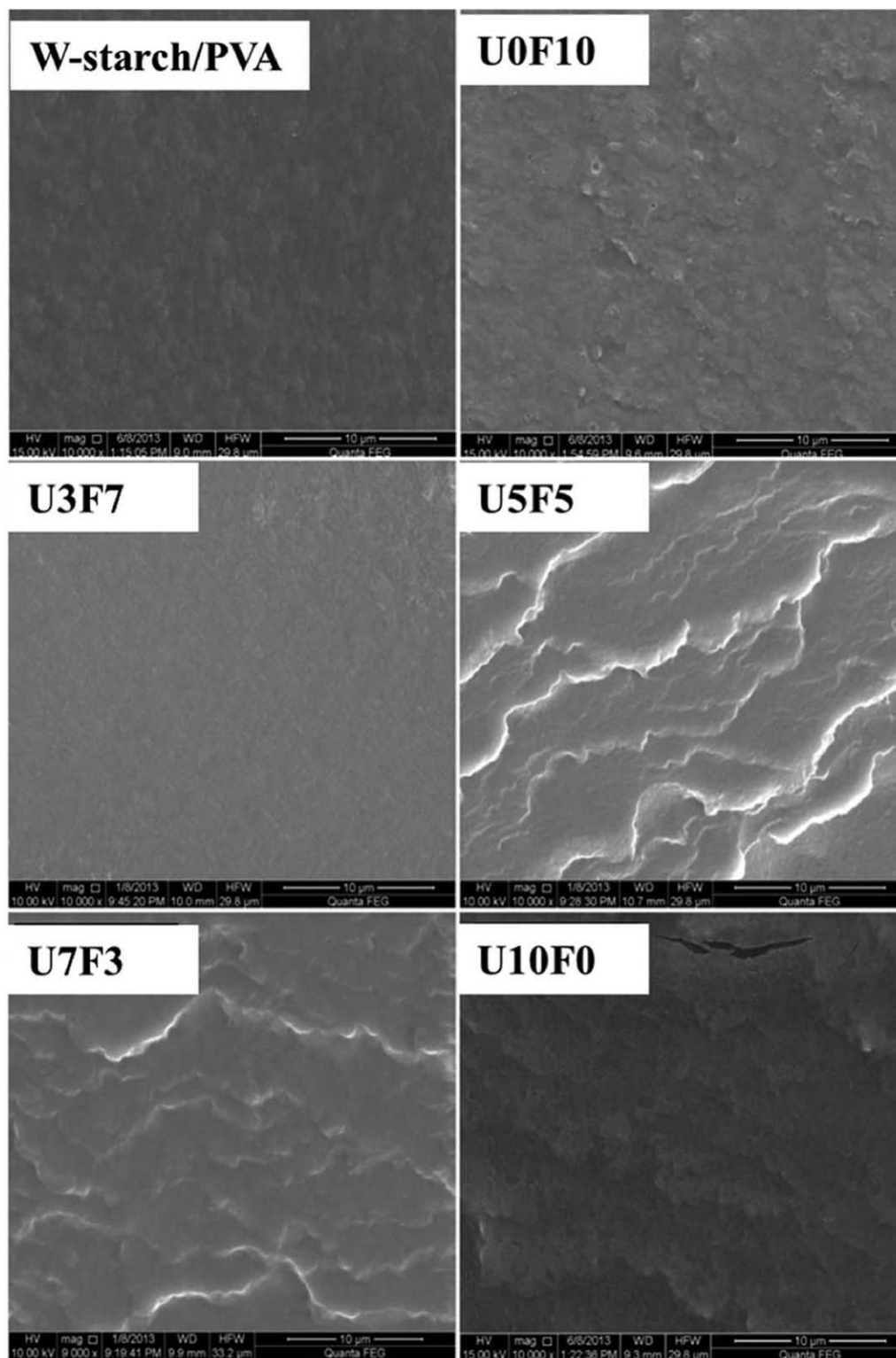| Sample	T_c	T_m	ΔH_m
U10F0	–	176.9	16.6
U7F3	–	179.8	20.4
U5F5	–	182.3	25.6
U3F7	–	182.5	26.8
U0F10	150.8	186.5	28.8
W-starch/PVA	191.5	202.9	40.2
W-starch	–	–	–
W-PVA	190.3	210.0	59.6

Figure 5. Micrographs of cross-section of W-starch/PVA blends and starch/PVA blends containing urea and formamide.

crystal structure. For W-starch/PVA blend, a broad melting peak at 202.9°C was observed, which was ascribed to the PVA component of the blend. Compared to W-PVA, the T_m (melting temperature) was lower and the melting peak became broad due to the interactions of starch and PVA molecules.

The T_m of the blends containing urea and formamide was lower than that of the W-starch/PVA blend. It was due to the facilitation of molecular motion ability of both urea and formamide plasticizers. Moreover, both the T_m and the melting enthalpy (ΔH_m) of the blends gradually decreased with the
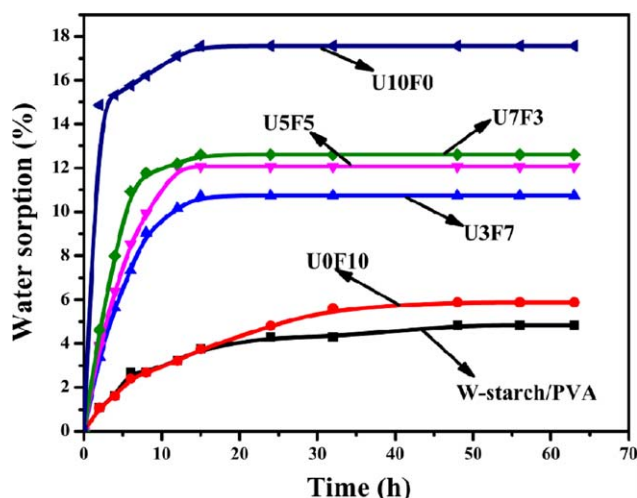
Figure 6. The water-uptake properties of starch/PVA blends at 58% relative humidity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increase of urea, indicating the decrease of crystallinity of the blends.

Scanning Electron Microscopy

Micrographs of cross-section of starch/PVA blends without and with urea and formamide are shown in Figure 5. Due to the high shear and temperature conditions in presence of plasticizers and water, native starch granules and PVA were molten or physically broken up into small fragments leading to formation of a continuous phase. The micromorphology of W-starch/PVA was extremely heterogeneous, indicating the poor compatibility of the blend. The micrograph of the cross-section of U0F10 blend was also heterogeneous, indicating that formamide was not good plasticizer and could not improve the compatibility of the blend. However, the micrographs of the cross-section of the blends indicate gradually improved compatibility with the increase of urea. Especially when the ratio of urea and formamide was 5 : 5–7 : 3, plasticizers had synergistic effects and the compatibility of the blend was highly improved. In addition,

the micrographs of the cross-section were filled with many raised structures, indicating rough fracture of the blends.

Water-Uptake Properties

The water-uptake properties of starch/PVA blends are shown in Figure 6. The water sorption property is useful for providing insight into the interactions of starch/PVA materials. As shown in Figure 6, the sorption of water quickly increased before 20 h, and then reached equilibrium for all starch/PVA samples. The water sorption trend of U0F10 blend was similar to that of W-starch/PVA. However, when urea was added, the rate of water absorption increased while the time to equilibrium became short indicating that the blends containing more urea was more sensitive to water. Urea could permeate into PVA molecules, and disrupt the crystal structures of PVA, resulting in the increased water absorption at equilibrium. The sorption of water molecules onto the external surface and amorphous regions is fast, while the sorption into inner surface and crystallites is relatively slow.

Mechanical Properties

Typical (a) stress–strain curves and (b) mechanical properties (b) of starch/PVA blends are shown in Figure 7. For W-starch/PVA blend, tensile strength and Young's modulus were higher but the elongation at break was very low, indicating rigid and fragile character of the blends, which may be caused by the high crystallinity and poor compatibility between starch and PVA. Moreover, for the U0F10 blend, the tensile strength and Young's modulus slightly decreased, and the elongation at break increased a bit compared to the W-starch/PVA blend. It also proves that formamide had poor plasticizing effect and could not improve the flexibility of starch/PVA blend. However, when urea was added, the tensile strength and Young's modulus were greatly decreased, and the elongation at break dramatically improved. Urea was a better plasticizer, which could improve the flexibility of starch/PVA blend.

As shown in Figure 7(b), the tensile strength and Young's modulus of the blends gradually decreased with the increase of urea. And the elongation at break and energy to fracture increased initially, reached a maximum, and then decreased. It could be concluded that urea and formamide had synergistic effects on starch/PVA blends. Urea could plasticize the matrix effectively,
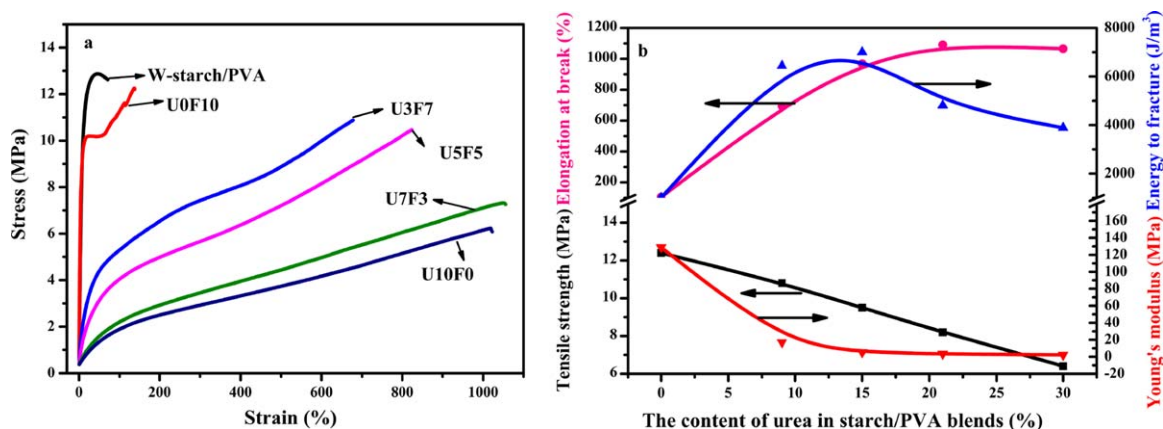

Figure 7. Typical (a) stress–strain curves and (b) mechanical properties of W-starch/PVA and starch/PVA blends containing urea and formamide at 58% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
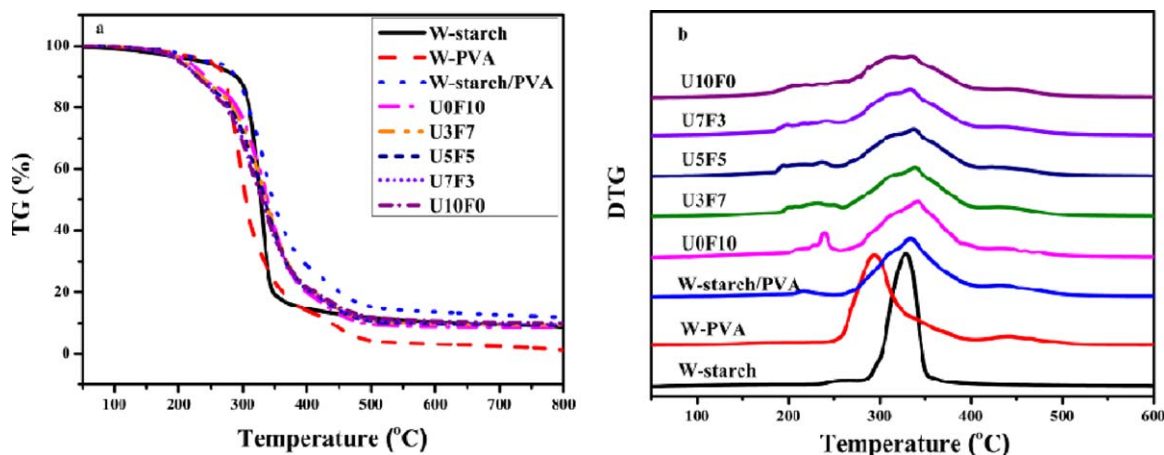
Figure 8. The (a) TG and (b) dTG curves of W-starch, W-PVA, W-starch/PVA, and starch/PVA blends containing urea and formamide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

whereas formamide could improve the stability of the plasticizing system. As a result, good flexibility of the blends was obtained when the ratio of urea and formamide was in the range of 5 : 5–7 : 3. For instance, the elongation at break of U7F3 was about 1091%, which was much higher that 76.9% of blends without urea and formamide plasticizers. Therefore, we could conclude that the sheets with more urea possessed higher flexibility due to the better plasticizing effect of urea, decreased crystallinity of the blends, as well as the increased moisture. Also the flexibility was much higher than results in the previously reported literatures.[26,27] Especially, the elongation at break of the blends U7F3 was several times much more than the reported results.

TG Analysis

The (a) TG and (b) dTG curves of W-starch, W-PVA, W-starch/PVA, and starch/PVA blends containing urea and formamide are shown in Figure 8. For W-PVA, the majority of mass loss took place at about 300°C, followed by a further smaller mass loss at around 440°C, which were attributed to the acetate group elimination at lower temperatures followed by a breakdown of polymer backbone at higher temperatures.[28] For W-starch, the degradation of starch macromolecules mainly occurs at 290–370°C. The T_d (degradation temperature corresponding to maximum degradation peak) of W-starch was higher than that of W-PVA. This could be due to the fact that starch was originally built up of cyclic-D-glucose with thermally stable cyclic hemiacetal structure.

For the blends, the initial decomposition below 250°C mainly involved the vaporization of volatiles including urea and formamide. The degradation peak on dTG curves of PVA and starch combined and the blends exhibited a sharp weight loss at 250–500°C. The blends containing urea and formamide exhibited lower thermal stability compared with W-starch/PVA for the lower residue weight after the thermodegradation, resulting by the evaporation of plasticizers.

CONCLUSIONS

The starch/polyvinyl alcohol (PVA) bioblends containing urea and formamide as plasticizers were prepared through melt proc-

essing in the presence of water. The plasticizers could form strong hydrogen bonds with starch/PVA molecules. Urea exhibited better plasticizing effect than formamide. Urea also could greatly destroy the crystal structure of PVA component in the blends, resulting in the decreased crystallinity of the blends. Formamide acted as a good solvent for urea and could resist separating from the blends. Without urea and formamide plasticizers, poor compatibility between starch and PVA was observed. The micrographs of the cross-section of the blends indicated gradually improved compatibility with the increase of urea and formamide, resulting in good flexibility of the blends. Therefore, the incorporation of both urea and formamide into starch/PVA blends could exhibit synergistic effects to ensure the blends with both good plasticizing effect and the stability of the plasticizing systems.

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