



N-(2-Hydroxypropyl)formamide and N-(2-hydroxyethyl)-N-methylformamide as two new plasticizers for thermoplastic starch

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ABSTRACT

N-(2-Hydroxypropyl)formamide (HPF) and N-(2-hydroxyethyl)-N-methylformamide (HMF) were used independently as new plasticizers for corn starch to prepare thermoplastic starch (TPS). The hydrogen bond interaction between HPF (or HMF) and starch was proven by Fourier-transform infrared spectroscopy. By scanning electron microscopy, starch granules were shown to be completely disrupted and homogeneous materials were obtained. The crystallinity of corn starch, HPF-plasticized TPS (PTPS) and HMF-plasticized TPS (MTPS) was characterized by X-ray diffraction. The crystallinity of TPS was affected by the structure of plasticizer. The water resistance of PTPS was better than that of MTPS. At medium relative humidity (RH), both tensile strength and elongation at break of PTPS were higher than those of MTPS. At high RH, the elongation at break of PTPS was higher than that of MTPS, while the tensile strength of PTPS was close to that of MTPS.

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1. Introduction

The improper disposition of the enormous volume of petroleum-derived plastics leads to environment pollution and raises the question how to replace them with natural, biodegradable and renewable resources. Currently, much research is devoted to starch, because it is inexpensive and abundant (Ma & Yu, 2004). Starch commonly exists in the form of granules with about 15–45% crystallinity. The development and production of biodegradable thermoplastic starch (TPS) is important to reduce the total amount of plastic waste. During the thermoplastic process, plasticizers play an indispensable role because the plasticizers could form the hydrogen bonds with starch, replacing the strong intra- and intermolecular hydrogen bonds in starch, thus resulting in plasticization. Generally, polyols are used as plasticizers for TPS, such as glycerol (Forsell, Mikkilä, Moates, & Parker, 1997), glycol (Da Róz, Carvalho, Gandini, & Curvelo, 2006), xylitol (Tristao de Andrade & Rocha de Souza, 2004), sorbitol (Wang, Shogren, & Carriere, 2000) and sugars (Barrett, Kaletunc, Rosenburg, & Breslauer, 1995). Amides such as urea (Stein & Greene, 1997), formamide (Ma & Yu, 2004) and ethylenebisformamide (Yang, Yu, & Ma, 2006) promote

the plasticization of starch, too. However, the properties of TPS do not meet what people expect. The type of plasticizer influences the properties of TPS. In views of the application and development of starch materials, it is very important to prepare new nontoxic plasticizer, which is used to produce TPS with desirable properties. Some work has been done to research the relationship of plasticizers structure and TPS properties (Stein, Gordon, & Greene, 1999). It is also important to study the relationship of plasticizers structure and TPS properties when developing new plasticizers.

Hydroxyalkylformamides (HAF) can serve as physiologically harmless humidifiers for cosmetics (Coupland & Smith, 1986) or are used for the impregnation of tire-cord made from nylon (Kibler & Richard, 1973). N,N-Bis(2-hydroxyethyl)formamide (BHF) (Dai, Chang, Yu, & Ma, 2008) and N-(2-hydroxyethyl)formamide (HF) (Dai, Chang, Peng, Yu, & Ma, 2009) belonging to HAF can be used as efficient plasticizers for corn starch to prepare TPS. In order to show that HAF can be used extensively as plasticizers for corn starch, two new plasticizers from HAF for corn starch, N-(2-hydroxypropyl)formamide (HPF) and N-(2-hydroxyethyl)-N-methylformamide (HMF), were studied with emphasis on the structure of plasticizer to TPS crystallinity. HPF and HMF are used to prepare HPF-plasticized TPS (PTPS) and HMF-plasticized TPS (MTPS), and the preparation and characterization of PTPS and MTPS in terms of FT-IR, morphology, XRD, water vapor absorption and mechanical properties are reported.

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2. Experimental

2.1. Materials

Corn starch (7.62% moisture) was obtained from the Langfang Starch Company (Langfang, Hebei, China). Glycerol and ethyl formate (analytical grade) were purchased from Tianjin Chemical Reagent Ltd. (Tianjin, China). 1-Amino-2-propanol and 2-(methylamino)ethanol (analytical grade) were purchased from TCI Development Co., Ltd. (Shanghai, China).

2.2. Synthesis of HPF and HMF

One mole of 1-amino-2-propanol (or 2-(methylamino)ethanol) was introduced into a 500 mL flask equipped with a stirrer, a reflux condenser, a dropping funnel and a thermometer. The flask was cooled to 20 °C in an ice bath and then 1 mol of ethyl formate was added in 30 min. The reaction mixture was stirred at 60 °C for 1 h, and the progress was monitored with thin layer chromatography (TLC). Then the ethanol formed as byproduct was removed from the mixture under reduced pressure at 60 °C. Subsequently the mixture was cooled to 20 °C in an ice bath, followed by addition of 0.05 mol of ethyl formate. The reaction mixture was stirred for 0.5 h at 60 °C, and then the byproduct ethanol evaporated under reduced pressure at 60 °C. The residue was cooled to 20 °C in an ice bath, followed by addition of 0.05 mol ethyl formate. The reaction mixture was stirred for another 0.5 h at 60 °C and then heated under reduced pressure at 105 °C until the mass of the liquid became constant. The purity was 97% (if the substrate was 2-(methylamino)ethanol, the purity of the liquid was 94%) as determined by column chromatography on neutral aluminum oxide (200–300 mesh) eluted with mixture of dichloro-

methane and methanol. The yield of HPF was 97%, and the yield of HMF was 94%.

¹H NMR spectra were measured on an INOVA 500 MHz spectrometer (Varian, Palo Alto, CA, USA) using TMS as internal standard and CD₃SOCD₃ as solvent. The IR spectra (KBr pellets) were recorded with an FTS3000 IR spectrometer (BioRad, Hercules, CA, USA). Mass spectra were determined on an LCQ Advantage MAX spectrometer (ESI).

2.2.1. Data for HPF and HMF

HPF. $\nu_{\max}$ (KBr): 3302 (OH), 2976 (—CH₃), 2932 (—CH₂—), 2880 (—CH₂—), 1665 (C=O) cm⁻¹; ¹H NMR (CD₃SOCD₃, δ ppm): 7.987–7.847 (m, 2H, HCONH), 3.648–3.517 (m, 1H, CHO), 3.399 (br, 1H, OH), 3.050–2.949 (m, 2H, CH₂N), 1.003–0.978 (m, 3H, CH₃), m/z (%): 104 (MH⁺, 68), 126 (MNa⁺, 100).

HMF. $\nu_{\max}$ (KBr): 3418 (OH), 2930 (—CH₂—), 2874 (—CH₂—), 1661 (C=O) cm⁻¹; ¹H NMR (CD₃SOCD₃, δ ppm): 7.975 (s, 1H, HCON), 7.915 (s, 1H, HCON), 3.473–3.375 (m, 6H, CH₂OH), 3.268–3.231 (m, 4H, CH₂N), 2.920 (s, 3H, CH₃), 2.726 (s, 3H, CH₃), m/z (%): 104 (MH⁺, 31), 126 (MNa⁺, 100).

2.3. Preparation of HPF-plasticized TPS (PTPS) and HMF-plasticized TPS (MTPS)

The plasticizer was blended with corn starch using a high speed mixer GH-100Y (Beijing Plastic Machinery Factory, Beijing, China) at 3000 rpm for 2 min, and then stored overnight. The mass ratios of plasticizer to corn starch (7.62% moisture content) were 25:100, 30:100 and 35:100, respectively. PTPS and MTPS were prepared as following. The mixtures were manually fed into the single-screw plastic extruder SJ-25(s) (screw ratio $L/D = 25:1$, Beijing Plastic Industry Combine Corporation, Beijing, China) with a screw speed

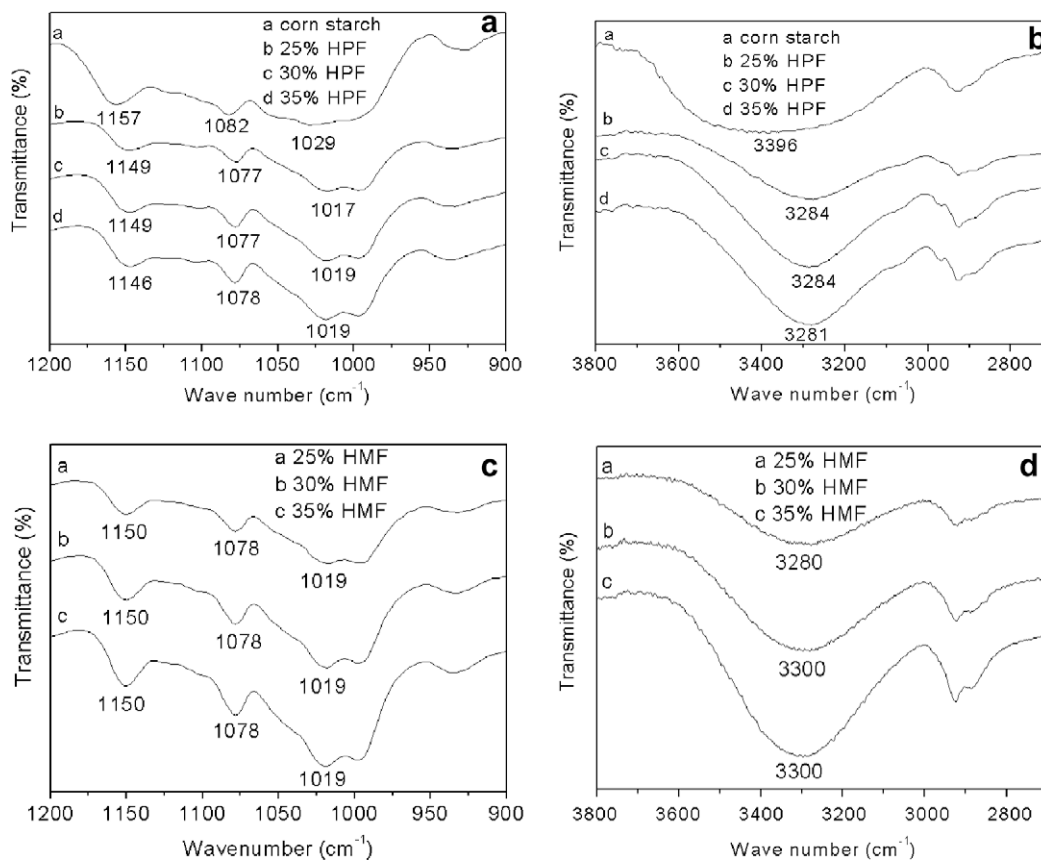


Fig. 1. FT-IR spectra of (a) corn starch and PTPS, (b) corn starch and PTPS, (c) MTPS and (d) MTPS.

of 15 rpm. The temperature profile along the extruder barrel was 130 °C, 125 °C, 130 °C and 130 °C (from feed zone to die). The die was a round sheet with the diameter 3 mm holes.

2.4. Fourier-transform infrared (FT-IR) spectroscopy

The IR spectra were measured with a FTS3000 IR Spectrum Scanner (BioRad, Hercules, CA, USA). The MTPS and PTPS samples were pressured to transparent slices at 10 MPa and 100 °C using the flat sulfuration machine (a compression molder), and measured in reflection mode.

2.5. Scanning electron microscopy (SEM)

Corn starch and the fracture surfaces of the PTPS and MTPS samples were investigated with a scanning electron microscope Phillips XL-3 (FEI Company, Hillsboro, Oregon, USA) operated at an acceleration voltage of 20 kV.

Starch powders were suspended in acetone. The suspension was applied on a glass slide, dried, and then vacuum-coated with gold for SEM. The conditioned PTPS and MTPS samples were cryo-fractured in liquid nitrogen. The fracture sections were vacuum-coated with gold for SEM.

2.6. X-ray diffraction (XRD)

The extruded PTPS and MTPS strips were pressed to the slices with a flat sulfuration machine (Beijing Plastic Machinery Factory) and the slices were placed in a sample holder for X-ray diffractometry. The corn starch powders were packed tightly in the sample holder. X-ray diffraction patterns were recorded in the reflection mode at an angular range of 10–30° (2 θ) at the ambient temperature by a Rigaku D diffractometer (Japan) operated at the Cu/K α radiation.

2.7. Water vapor absorption

2.7.1. Measurement of water contents of freshly prepared PTPS and MTPS

The bars of samples were cut into small pieces, and the pieces were weighed immediately. They were then dried in an oven at 105 °C overnight. The original water content (k) of PTPS or MTPS was calculated as follows:

$$k = \frac{w_1 - w_2}{w_1} \times 100\% \quad (1)$$

Here w_2 was the mass of the dried sample and w_1 was the mass of the sample before drying.

2.7.2. Measurement of water contents of PTPS and MTPS stored at different relative humidities (RHs)

The bars of PTPS and MTPS were stored in closed containers in the presence of different salt solutions, i.e., saturated K₂CO₃ and CuCl₂ solutions, which provided RHs of 44% and 68%, respectively, (Godbillot, Dole, Joly, Rogé, & Mathlouthi, 2006) at 20 °C. The water contents of PTPS and MTPS at different RHs were calculated on the basis of mass of PTPS and MTPS absorbing water. The data were averages of three specimens.

2.8. Mechanical testing

Mechanical testing (National standard of China GB1040–79) of samples was determined in the AX M350-10KN Materials Testing Machine (Testometric, Rochdale, UK) at a crosshead speed of 10 mm/min. The data were averages of five specimens.

3. Results and discussions

3.1. FT-IR analysis

The IR spectra of corn starch, PTPS and MTPS are shown in Fig. 1. The peak wave number 1157 cm⁻¹ was ascribed to the C–O bond stretching of the C–O–H group in starch. The characteristic peaks at 1082 cm⁻¹ and 1029 cm⁻¹ were attributed to C–O bond stretching of the C–O–C group in the anhydroglucose ring of starch (Fang, Fowler, Tomkinson, & Hill, 2002). The peak wave number 3396 cm⁻¹ was attributed to starch O–H bond stretching. In both

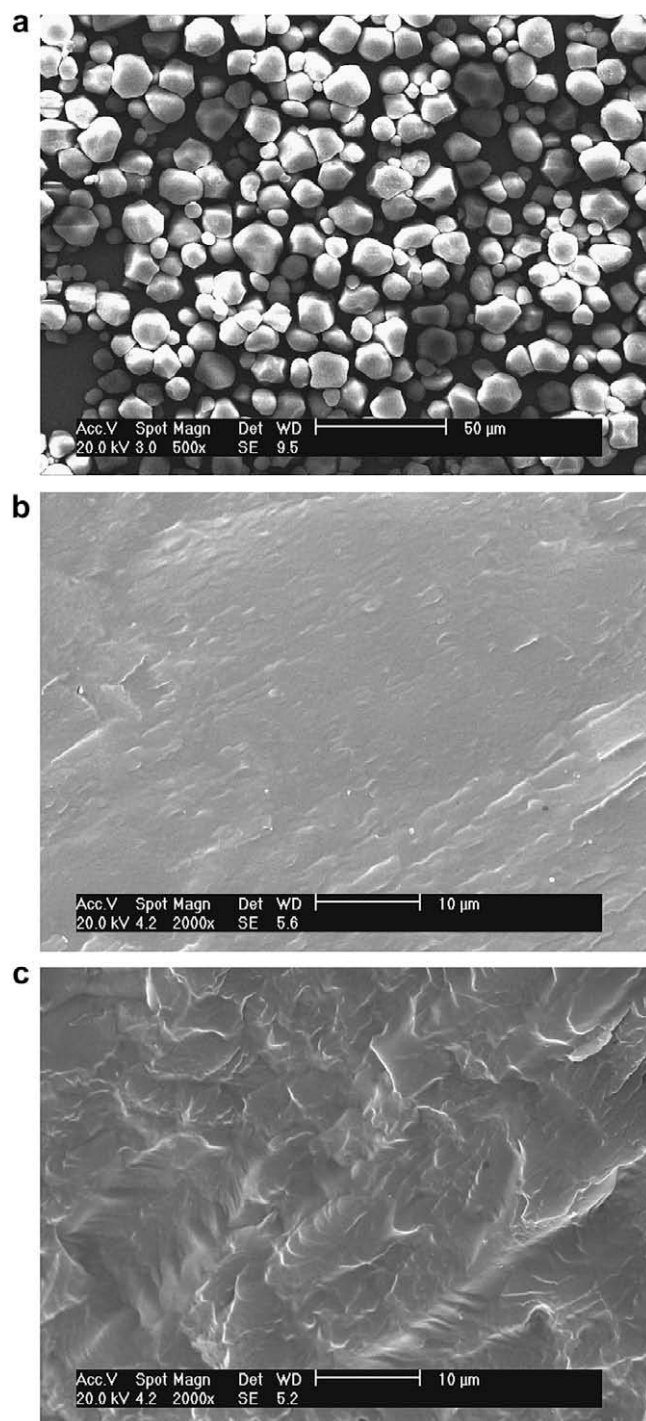


Fig. 2. SEM micrograph of (a) corn starch, (b) PTPS containing 30% HPF and (c) MTPS containing 30% HMF.

PTPS and MTPS, all peaks shifted to lower wave numbers. For example, the peak 1157 cm^{-1} in starch shifted to around 1149 cm^{-1} in PTPS and 1150 cm^{-1} in MTPS, respectively.

The analysis of FT-IR spectra of the blends enabled the hydrogen bond interactions to be identified (Aoi, Takasu, Tsuchiya, & Okada, 1998). Hydrogen bonds between plasticizer and starch were directly related to the wave number shift of the stretching bands of functional groups in starch. The lower the peak wave number was, the stronger the interaction was (Pawlak & Mucha, 2003). All these results indicated that stronger hydrogen bonds were formed between HPF (or HMF) and starch compared with intra- and intermolecular hydrogen bonds in starch. Due to the presence of the groups —O—H and —CO—N in HPF (or HMF), stable hydrogen bonds were formed between HPF (or HMF) and starch, which could weaken the intra- and intermolecular hydrogen bonds in starch to result in plasticized starch.

3.2. Scanning electron microscopy (SEM)

The morphology structures of starch in its native form and in the extruded PTPS and MTPS are shown in Fig. 2. Corn starch was granular, whereas PTPS and MTPS were homogeneous materials. Due to the high shear and temperature conditions with the action of plasticizer, the intermolecular and intramolecular hydrogen bonds in starch granules were weakened and disrupted by HPF (or HMF) and homogenous materials were obtained.

3.3. X-ray diffraction analysis (XRD)

The X-ray diffraction patterns of corn starch, PTPS, and MTPS equilibrated at ambient conditions (RH $\sim 50\%$) for 7 days are shown in Fig. 3. The crystallinity of corn starch was ascribed to A-type with crystal lattice of double helical structure. V_A -type crys-

tallinity was formed in PTPS (Fig. 3a, line c), while E_H and V_A types of crystallinity were formed in MTPS (Fig. 3b, line b) (van Soest, Hulleman, de Wit, & Vliegenthart, 1996). Both E_H and V_A types of crystallinity are single helical structure, and E_H crystallinity differs from V_A crystallinity in the arrangement of the single helices. During the processing, the plasticizer (HPF or HMF) penetrated into starch granules and weakened starch intermolecular and intramolecular hydrogen bonds, thus destroying the crystallinity of corn starch. A-type crystallinity of corn starch disappeared, and other crystalline patterns were formed in PTPS and MTPS.

van Soest et al. (1996) reported that V_H crystallinity was formed in TPS. However, there was no V_H crystallinity formed in PTPS and MTPS in this study. According to van Soest et al. (1996), V_H crystallinity was found in extruded and compression molded TPS containing more than 10% (w/w) water, whereas E_H and V_A crystallinity were formed in materials containing relatively little water content such as $<10\%$ (w/w). Due to the low moisture content (7.62%) of starch used in this study, V_A crystallinity was formed in PTPS, E_H and V_A crystallinity were formed in MTPS, and there was no V_H crystallinity formed in PTPS and MTPS. Nevertheless, the crystallinity of PTPS was different from that of MTPS. It can be concluded that the crystallinity of TPS not only affected by the water content, but also affected by the structure of plasticizer.

According to van Soest et al. (1996), E_H structure of TPS was formed in the presence of bulky complexing agents like acetone or *tert*-butanol. Therefore the formation of E_H crystallinity formed in MTPS was attributed to the presence of bulky HMF. Because HPF was not as bulky, E_H crystallinity was not formed in PTPS.

When an N atom was attached to a double bond (as in $>\text{N—C=O}$), its lone pair electron can delocalize over the π system forming an approximately planar three-atom framework (Pontes, Basso, & dos Santos, 2007). Due to the barrier to internal rotation around the N—C(O) bond in amides, H, O, C, N and atoms attaching

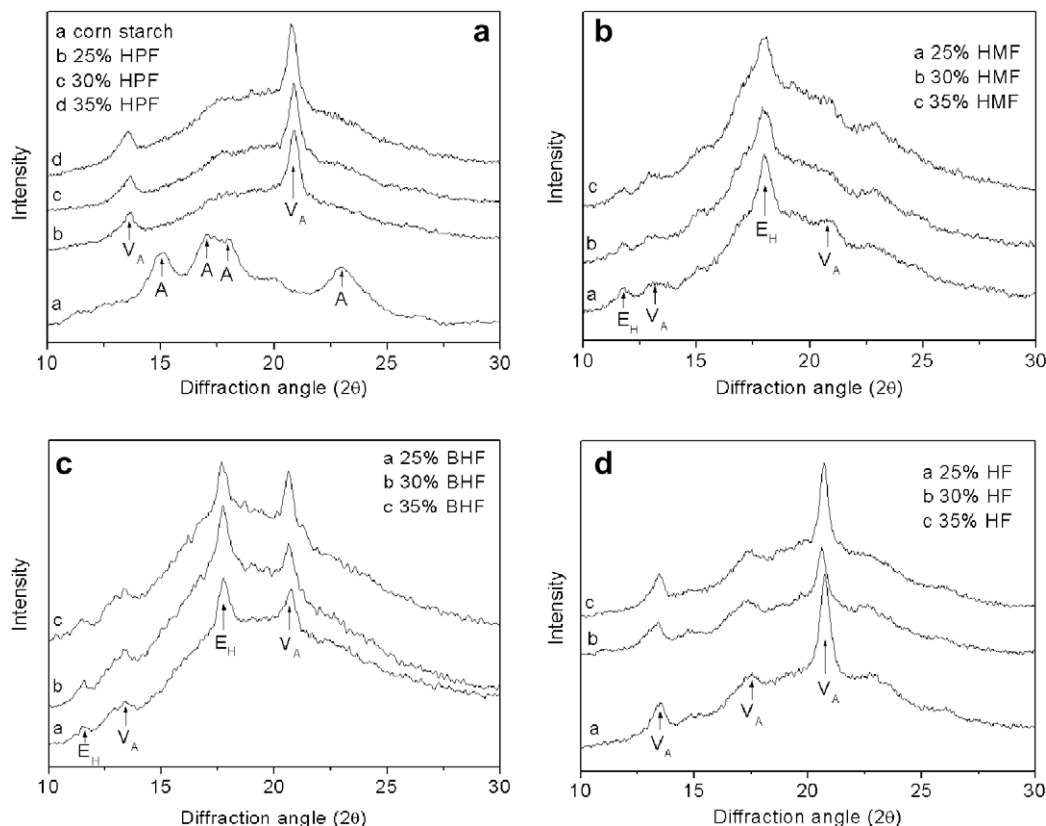


Fig. 3. Diffractogram of (a) corn starch and PTPS, (b) MTPS, (c) BTPS and (d) HTPS exposed to the air for 7 days.

to N formed a bulky group in HAF. Compared with hydroxymethyl group, amide group was more bulky. Methyl attached to N of amide led to the bulky effect that induced the formation of E_H crystallinity in TPS. In contrast, methyl attached to C of hydroxymethyl group could not lead to the bulky effect to induce E_H -type crystallinity. Therefore, E_H crystallinity was formed in MTPS, but only V_A crystallinity was formed in PTPS.

In our previous study, E_H and V_A crystallinity (Fig. 3c) were formed in BHF-plasticized TPS (BTPS) (Dai et al., 2008), V_A crystallinity (Fig. 3d) was formed in HF-plasticized TPS (HTPS) (Dai et al., 2009). Compared with HF, BHF was more bulky. Thus, E_H and V_A crystallinity were formed in BTPS, but only V_A -type crystallinity was formed in HTPS. E_H crystallinity in BTPS was due to the presence of bulky BHF too.

Compared with HF, HMF had a methyl group attached to N of amide group, and was bulky enough to induce formation of E_H crystallinity. Unlike HMF, HPF is not as bulky as HMF, so only V_A -type crystallinity was formed in PTPS. The HAFTPS crystallinity was affected by the structure of plasticizer HAF.

3.4. Water vapor absorption

Because TPS was sensitive to humidity, it is important to evaluate the influence of humidity on TPS properties. The water contents of PTPS and MTPS stored at 44% and 68% RHs up to 25 days were examined, and the results are shown in Fig. 4. At the same RH, the equilibrium water content of MTPS was greater than that of PTPS. The maximum water contents of MTPS and PTPS stored at RH 68% for 25 days were 14.1%, 16.6%, 18.1% and 13.6%, 14.4%, 15.4% (corresponding to the plasticizer contents 25%, 30%, and 35%), respectively. The water resistance of PTPS was better than that of MTPS. The water resistance of MTPS and PTPS decreased with increasing plasticizer content.

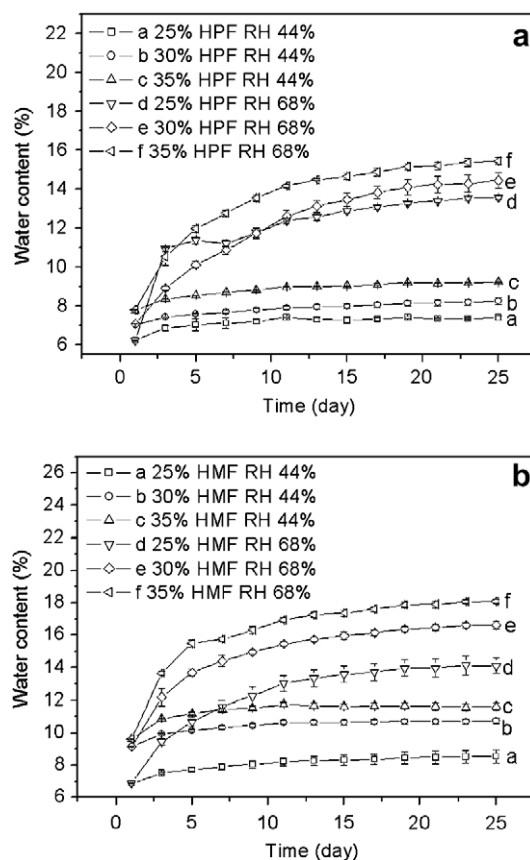


Fig. 4. Water contents of (a) PTPS and (b) MTPS as function of storage time at 44% and 68% RH.

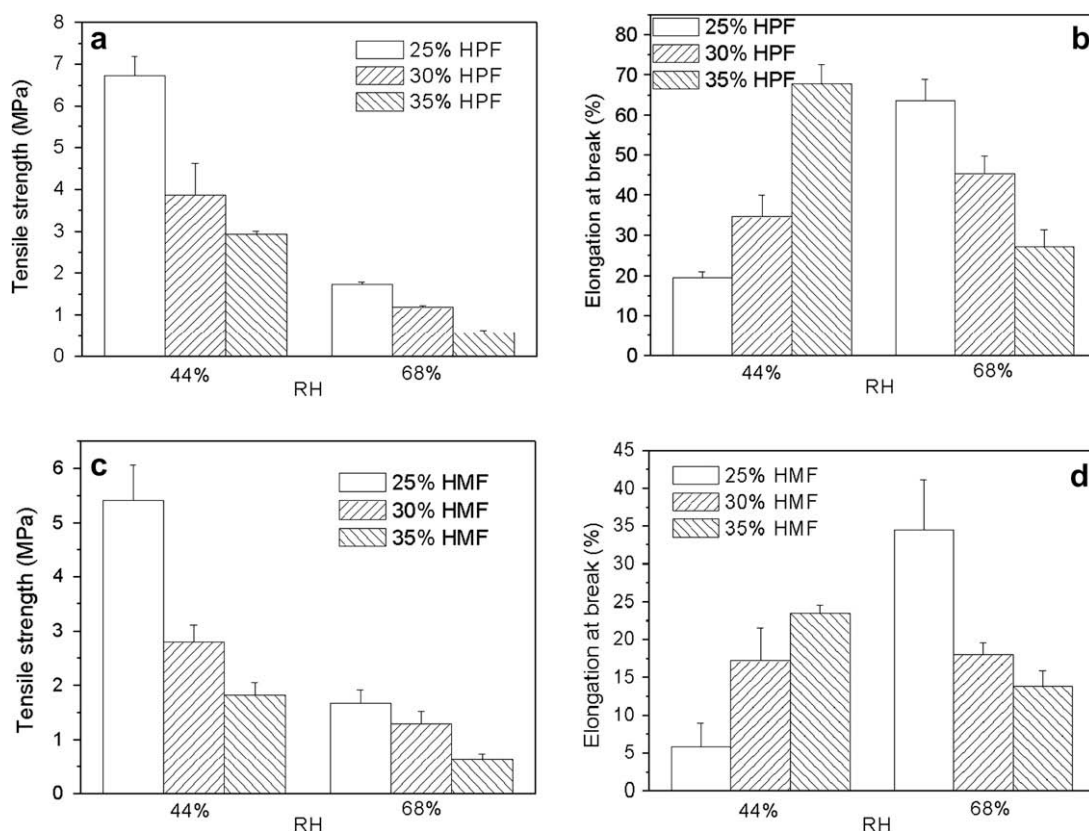


Fig. 5. (a) Tensile strength of PTPS, (b) elongation at break of PTPS, (c) tensile strength of MTPS and (d) elongation at break of MTPS stored at different RHs for 28 days.

3.5. Mechanical properties

The tensile strength and elongation at break of TPS stored at 44% and 68% RHs for 28 days were examined. At intermediate RH (44%), both tensile strength and elongation at break of PTPS were higher than those of MTPS (Fig. 5). The tensile strength and the elongation at break were 6.7 MPa and 19.6% for PTPS, and 5.4 MPa and 5.9% for MTPS when TPS containing 25% plasticizer was stored at 44% RH for 28 days. At high RH (68%), the tensile strength of PTPS was close to that of MTPS, whereas, the elongation at break of PTPS was higher than that of MTPS. For example, the tensile strength and the elongation at break were 1.8 MPa and 63.6% for PTPS, and 1.7 MPa and 34.6% for MTPS when TPS containing 25% plasticizer was stored at 68% RH for 28 days.

With increasing plasticizer content, the tensile strength of TPS decreased, whereas its elongation at break increased. For example, the tensile strengths of PTPS containing 25%, 30% and 35% of plasticizer were 6.7 MPa, 3.9 MPa and 2.9 MPa, respectively, after storage at 44% RH for 28 days. The elongations at break of PTPS containing 25%, 30% and 35% plasticizer were 19.6%, 34.7% and 67.9%, respectively. Plasticizer lowered the interaction of the molecules, thus decreasing the tensile strength. At the same time, it improved the movement of the segments and macromolecules, which led to the increase of the elongation at break.

When TPS was stored at 68% RH, the mechanical properties became poor. At the high RH, TPS absorbed too much water, which is an effective plasticizer and weakened the mechanical properties of PTPS and MTPS.

4. Conclusions

HPF and HMF were shown to be effective as novel plasticizers for corn starch. HPF (or HMF) formed strong and stable hydrogen bonds with starch, as shown by the analysis of the FT-IR spectra. From the analysis of SEM, starch granules were completely disrupted and became homogeneous. X-ray diffraction analysis indicated that A-type crystallinity of corn starch disappeared and starch was plasticized by HPF (or HMF). TPS crystallinity was affected by the structure of plasticizer. E_H crystallinity was formed in MTPS due to the presence of bulky plasticizer HMF. Only V_A crystallinity was formed in PTPS. PTPS showed better water resistance than MTPS. At intermediate RH, both tensile strength and elongation at break of PTPS were higher than those of MTPS. At high RH, the elongation at break of PTPS was higher than that of MTPS, while the tensile strength of PTPS was close to that of

MTPS. HAF including BHF, HF, HPF and HMF were novel, efficient plasticizers for thermoplastic starch and can be used for the study of the relationship between TPS properties and plasticizer structure.

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