



# Formamide and 2-hydroxy-*N*-[2-(2-hydroxy-propionylamino)-ethyl] propionamide (HPEP) as a mixed plasticizer for thermoplastic starch

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## ABSTRACT

As a plasticizer of starch, 2-hydroxy-*N*-[2-(2-hydroxy-propionylamino)-ethyl] propionamide (HPEP) is synthesized by the reaction of lactic acid and ethylenediamine. Melt extrusion processing is used to prepare thermoplastic starch by the mixed plasticizers of formamide and HPEP (FHTPS). Fourier Transform Infrared proves that the mixed plasticizers can form the interaction with C=O group of starch in FHTPS. Scanning Electron Microscope shows that formamide and original water are necessary to form the homogeneous FHTPS containing formamide/HPEP/original water (20/10/10). X-ray diffraction exhibits that the mixture of formamide and HPEP can effectively suppress starch re-crystallization, and the original water has no effect on starch re-crystallization when FHTPS are stored at RH 50% for 50 days. Water absorption testing shows that the more HPEP is, the better water resistance of FHTPS is. With the increasing of HPEP ratios, the tensile strength of FHTPS is increased while the elongation is decreased at the whole range of water contents.

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## 1. Introduction

Starch is a promising raw material because of its annual availability from many plants (Chen & Evans, 2005). In addition to being staple food, starch has recently gained interest as a renewable and biodegradable plastic (Wang, Zhang, Han, & Bai, 2009) because of the worldwide environment and resources problems resulted from petroleum-derived plastics (Averous, Fauconnier, Moro, & Fringant, 2000). Native starch commonly exists in a granular structure, which can be processed into continuous materials by both casting and thermoplastic extrusion processing. In the casting, granular starch is turned into gelatinized starch in the solution, and the film can be obtained after evaporating the solvent. Compared with solution casting, thermoplastic extrusion is a “green” and facile processing condition, in which starch granules are broken and the continuous phase is formed under the action of high temperature and shear by melt extrusion. During the thermoplastic process, water contained in starch and the plasticizers play an indispensable role (Hulleman, Janssen, & Feil, 1998; Wang, Shogren, & Carriere, 2000). The plasticizers and water can form the hydrogen bonds with starch, reduce intermolecular hydrogen bonding of starch, and turn starch into thermoplastic starch (TPS).

TPS are usually plasticized by hydroxyl compounds, and polyols are often cited as traditional plasticizers for starch-based materials.

The different polyols such as glycerol, xylitol (Talja, Helen, Roos, & Jouppila, 2008), sorbitol (Da Roz, Carvalho, Gandini, & Curvelo, 2006), glucose (Ma, Yu, He, & Wang, 2007), fructose, mannose, galactose and maltitol (Zhang & Han, 2006) are used for plasticizing starch (Mathew & Dufresne, 2002). However, TPS plasticized by polyols are thought to tend to starch re-crystallization after being stored for a period of time and the re-crystallization embrittles TPS (Van Soest & Knooren, 1996). Among of polyols, glycerol is a typical plasticizer of starch. We have investigated the feasibility of small substance with amide group such as formamide, acetamide and urea to plasticize starch (Ma & Yu, 2004a). These plasticizers can restrain starch re-crystallization because of the stronger hydrogen bond interaction between amide groups and starch than polyols. Subsequently, ethylenebisformamide with double-amide group is synthesized for the preparation of TPS (Yang, Yu, & Ma, 2006). Among of them, formamide is a typical plasticizer of starch. Recently, as a novel and nontoxic plasticizer containing both amide and hydroxyl groups, HPEP is synthesized for TPS. Since both formamide and glycerol are good solvents for HPEP, a combination of HPEP and formamide (or glycerol) may be a better plasticizer. TPS plasticized by the mixture of HPEP and glycerol has exhibited better mechanical properties and water resistance than TPS plasticized by glycerol (Zhang, Chang, Wu, Yu, & Ma, 2008). In this paper, HPEP and formamide are used as a mixed plasticizer to prepare TPS (FHTPS). The processing and characterization of FHTPS are described in terms of the hydrogen bonding interaction between plasticizer and starch, the effect of original water contents and

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HPEP ratios on the plasticization and the crystalline, water absorption and mechanical properties.

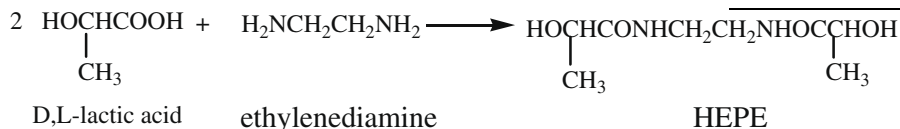
## 2. Experimental

### 2.1. Materials

Corn starch is obtained from Langfang Starch Company (Langfang, Heibei, China). Formamide, ethylenediamine, D,L-lactic acid, anhydrous ethanol and THF of analytical grade from Tianjin Chemical Reagent Factory (Tianjin, China).

### 2.2. Synthesis of HPEP

HPEP is produced based on the method of Zhang et al. (2008) with some modifications. As a general procedure, 25 mol ethylenediamine is placed in a 1000-mL flask cooled in an ice-bath and 50 mol D,L-lactic acid is slowly added. Subsequently, the ice-bath is removed and the solution was heated to 120–140 °C for 3 h and then heated to 180–190 °C for 4 h. At the same time, the byproduct water evaporates under reduced pressure until there is no water distilled from the mixture. After the mixture is cooled to room temperature, it is re-crystallized from anhydrous ethanol and anhydrous THF (1/9 v/v) for pure HPEP with the yield of about 90%. The reaction is as follow:



### 2.3. Preparation of FHTPS

Formamide and HPEP are mixed as the plasticizers of FHTPS. The ratio of plasticizers and corn starch is 30:100 (w/w). Water is added into corn starch to adjust the original water contents. The mixed plasticizers are blended (3000 rpm, 2 min) with corn starch in the high speed mixer GH-100Y (Beijing Plastic Machinery Factory, Beijing, China), and then stored overnight. The mixtures are 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 of 15 rpm. The temperature profile of FHTPS along the extruder barrel is 145, 150, 150 and 145 °C (from feed zone to die). The die is a round sheet with five holes 3 mm in diameter. The extruded samples are conditioned in sealed polyethylene bags to maintain a stable water contents.

### 2.4. Fourier transform infrared (FTIR) spectroscopy

FHTPS samples are pressed to transparent slices (about 0.5 mm) at 10 MPa and 100 °C using the Flat Sulfuration Machine (a compression molder) (Beijing Plastic Machinery Factory). The FTIR spectra of the slices are measured in reflection mode with a Bio-Rad FTS3000 IR Spectrum Scanner (Hercules, CA, USA).

### 2.5. Scanning electron microscopy (SEM)

The fracture surfaces of FHTPS samples are investigated with the scanning electron microscope Philips XL-3 (FEI Company, Hillsboro, Oregon, USA), operating at an acceleration voltage of 20 kV. The samples are cryo-fractured in liquid nitrogen. The fracture faces are vacuum-coated with gold for SEM.

### 2.6. X-ray diffractometry

The extruded FHTPS strips are pressed to slices with a flat sulfuration machine and the slices are placed in a sample holder for X-ray diffractometry. Corn starch and HPEP powders are packed tightly in the sample holder. When FHTPS samples are stored at different relative humidities (RH 50% or 100%) for a period of time, X-ray diffraction patterns are recorded in the reflection mode at an angular range of 10–30° (2θ) at ambient temperature by a Rigaku D diffractometer (Tokyo, Japan) operated at the Cu Kα wavelength of 154.056 pm.

### 2.7. Water absorption

The water contents  $\alpha_0$  (dry basis) of FHTPS before the storage are determined gravimetrically by drying small pieces at 105 °C overnight. When FHTPS samples are stored for a period of time, water contents are calculated on the basis of original weight  $w_0$ , current weight  $w$  and  $\alpha_0$ . Water contents  $\alpha$  are calculated as follows:

$$\alpha = \frac{w}{w_0}(1 + \alpha_0) - 1$$

Native starch is dried at 105 °C overnight. When formamide, HPEP and dried starch ( $\alpha_0 = 0$ ) are stored for a period of time, water contents are calculated on the basis of original weight  $w_0$  and current weight  $w$ .

### 2.8. Mechanical testing

Samples are pressed with the flat sulfuration machine into the sheet. Testometric AX M350-10KN Materials Testing Machine is operated at a crosshead speed of 50 mm/min for tensile testing (ISO 1184–1983 standard). The data are averaged over 5 specimens. In order to analyze the effect of water contents on mechanical properties of FHTPS, they are stored at RH 50%, 75% and 100% for a period of time.

## 3. Results and discussion

### 3.1. FTIR

As the plasticizer, it should form hydrogen bonds with starch, replace the original interactions between the hydroxyl groups of the starch molecules, and thus make starch plasticization. The forms of the most probable hydrogen bonds between plasticizers (formamide or HPEP) and starch are shown in Fig. 1. The analysis of FTIR spectra of TPS enables hydrogen bond interactions to be identified (Ma & Yu, 2004a). Moreover, the lower the peak frequency of C—O group in starch is, the stronger the interaction between starch and plasticizers is. Both O=C, NH and OH groups of HPEP and O=C and NH<sub>2</sub> groups of formamide can form hydrogen bonds with starch. Fig. 2 exhibits FT-IR spectra for starch and FHTPS (at original water contents 10 wt%) with different weight ratios of formamide and HPEP. There are three characteristic peaks of starch between 900 and 1200 cm<sup>−1</sup>, attributed to C—O bond stretching (Fang, Fowler, Tomkinson, & Hill 2002). The peaks at around 1150 and 1080 cm<sup>−1</sup> are characteristic of C—O—H in starch, while the peak between 990 and 1020 cm<sup>−1</sup> is characteristic of the anhydroglucose

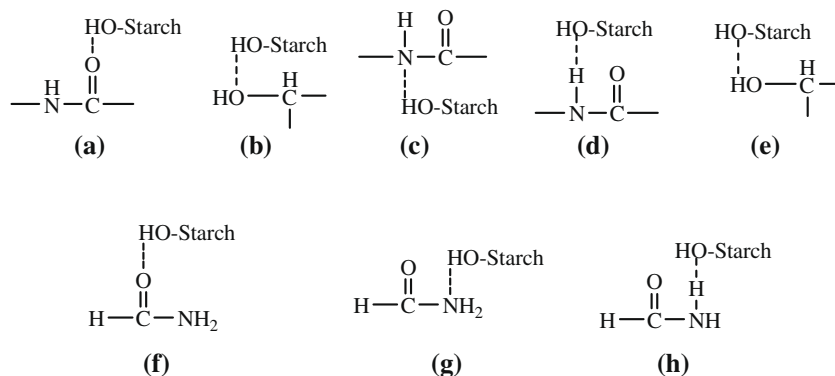


Fig. 1. Illustrations of the most probable forms of hydrogen bonds between HPEP (a–e) /formamide (f–h) and starch.

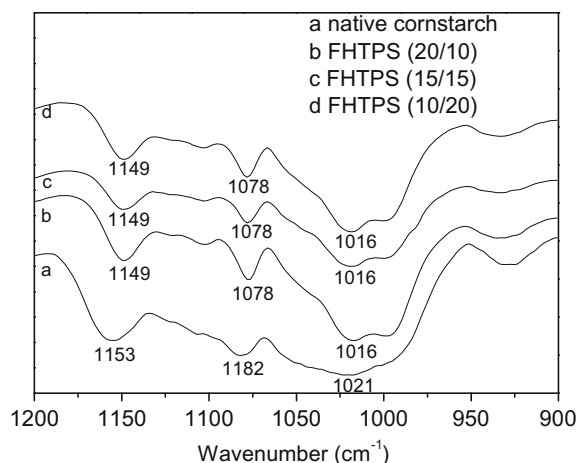


Fig. 2. The FT-IR of native corn starch and FHTPS with different weight ratios of formamide and HPEP (20/10), (15/15) and (10/20) at the same original water contents of 10%.

ring O—C stretch. As shown in Fig. 2, compared to three characteristic peaks of native starch, those of TPS locate at the lower wave number, and the double-peak appears at between 990 and 1020  $\text{cm}^{-1}$  instead of the single peak of native starch, because the mixture of formamide and HPEP can form the stable hydrogen bonds with both O of C—O—H and O of anhydroglucose ring O—C in starch molecules. Therefore, this phenomenon should be related to the stability and intensity of hydrogen bonds, which are newly formed between formamide/HPEP and C—O group of starch. However, the weight ratios of formamide and HPEP in FHTPS have little influence on the shift of these three characteristic peaks of starch. It illustrates that HPEP and formamide have the similar intensity of hydrogen-bond formation with starch molecules.

### 3.2. SEM

The mixture of formamide and HPEP can form stable hydrogen bond with starch by the analysis of FTIR spectra. Due to the high shear and temperature conditions with the action of plasticizers and water, native starch granules are molten or physically broken up into small fragments. A continuous phase is predicated to be formed under shear and pressure as a result. Fig. 3 reveals the microcosmic morphology of the extruded FHTPS with different weight ratios of formamide, HPEP and original water. Both the ratios of formamide/HPEP and original water contents affect the morphology of FHTPS.

As shown in Fig. 3a–c at the same original water content (10 wt%), a quantity of granules do not fuse into one continuous

phase for FHTPS containing formamide/HPEP (10/20 and 15/15), while no residual granular structure is present in the continuous phase for FHTPS containing formamide/HPEP (20/10). If formamide/HPEP (0/30) were used to plasticized starch, no homogeneous TPS would be obtained. Since the melting point of HPEP is about 145–147 °C, HPEP just melts at the processing temperature 150 °C. The hyperthermal processing can result in the thermal degradation of starch and the volatilization of plasticizer or water. At this condition, HPEP is difficult to diffuse into the granules of starch. It means that enough formamide is necessary to form the homogeneous FHTPS. As a good solvent for HPEP, formamide can dissolve it and the mixture of formamide and HPEP can diffuse into the granules of starch before melt extrusion processing.

As shown in Fig. 3c–e at the same weight ratios of formamide/HPEP (20/10), with the decreasing of original water contents from 10% to 0%, the more residual granular structures are observed. Actually, water is a good plasticizer for starch. The original water containing in starch will swollen the granules of starch, then other plasticizers are apt to infiltrate into the granules. Water is also a good solvent for HPEP.

### 3.3. X-ray

The effect of the weight ratios of formamide and HPEP on the X-ray diffraction patterns of newly prepared FHTPS and FHTPS stored for 50 days are shown in Fig. 4a and b, respectively. As shown in Fig. 4a, native cornstarch possesses the A-style crystallinity, while there is no obvious crystallinity in FHTPS. In the thermo-plastic processing, plasticizer molecules and water enter into starch particles and replace starch intermolecular and intramolecular hydrogen bonds and destruct the A-style crystallinity of starch. However, in FHTPS with formamide/HPEP (10/20), the tiny  $V_H$ -style crystallinity appear, which originate from the stress inducement during the thermal process and is a single-helical structure “inclusion complex” made up of amylose and plasticizer (Van Soest, Hulleman, de Wit, & Vliegenthart, 1996). Since formamide can effectively restrain the  $V_H$ -style crystallinity (Ma & Yu, 2004b), FHTPS with formamide/HPEP (20/10) exhibits no  $V_H$ -style crystallinity. When FHTPS are stored at RH 50% for 50 days (in Fig. 4b), there is no the re-crystallization of starch. The crystal peaks at around 26° are ascribed to HPEP crystallinity. The mixed plasticizers of formamide and HPEP can effectively suppress the re-crystallization of starch component at RH 50%. The hydrogen bond between starch and the mixed plasticizers can prevent starch molecules from interacting and crystallizing again during the storage time.

Fig. 5 reveals that the original water contents in native starch seem have little effect on the X-ray diffractograms of both newly

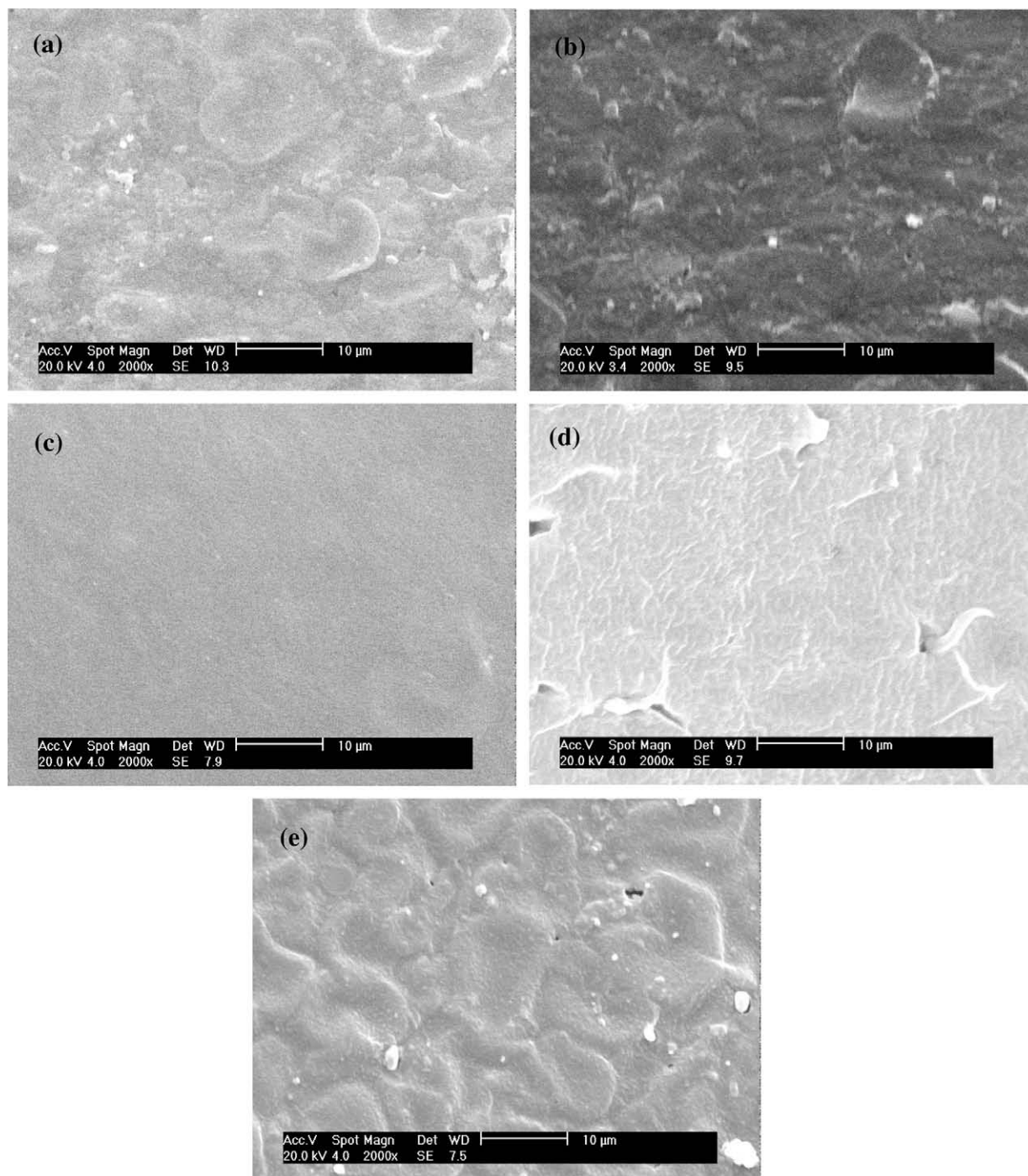


Fig. 3. SEM of FHTPS with the various weight ratios of formamide, HPEP and original water. (a) 10/20/10, (b) 15/15/10, (c) 20/10/10, (d) 20/10/5 and (e) 20/10/0.

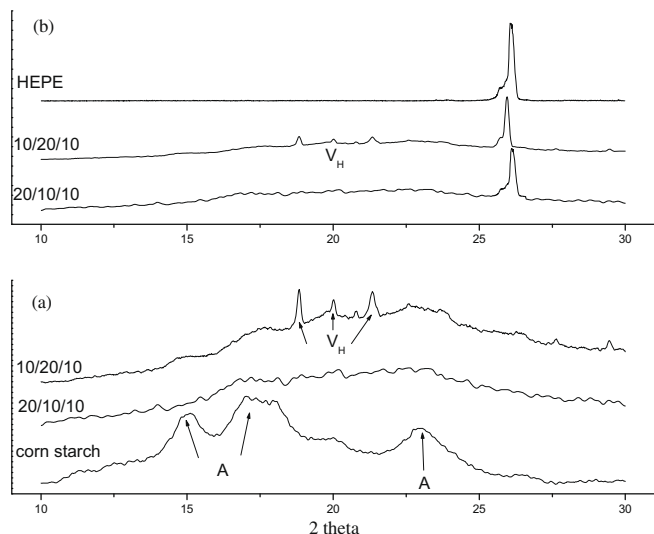
prepared FHTPS and FHTPS stored at RH 50% for 50 days, when the ratio of formamide and HPEP is 20/10. In views of the crystallinity of FHTPS, the ratio of formamide and HPEP is more important than the original water contents in native starch.

In addition, FHTPS with different ratios of formamide, HPEP and the original water will not exhibit any crystallinity including  $V_H$  and HPEP crystallinity, when FHTPS are stored at RH 100% for 50 days. These X-ray diffractograms are not shown here. The absorbed water at high RH can dissolve the HPEP crystallinity and destroy the interaction between amylose and plasticizer in “inclusion complex”.

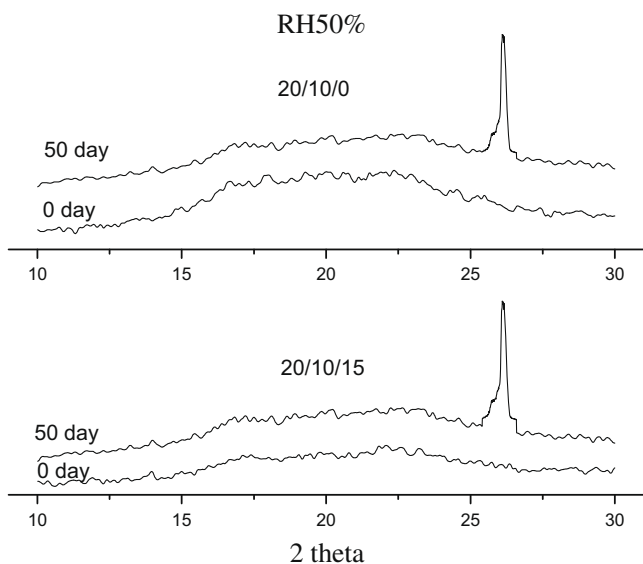
### 3.4. Water absorption

Water sensitivity is an important criterion for the applications of starch materials. Because TPS is made up of starch and plasticizers, water absorption of TPS mainly depends on water absorption of the plasticizer. Fig. 6 shows the relation of storage time and water contents of native corn starch, EHPE and formamide at RH = 100%. Water absorption of formamide can reach 200% in 20 days, while the equilibrium water contents for EHPE and corn starch are only about 50% and 20%, respectively.





**Fig. 4.** (a) The X-ray diffractograms of native corn starch and newly prepared FHTPS with the weight ratios of formamide and HPEP (20/10) and (10/20) at the same original water contents of 10%. (b) The X-ray diffractograms of FHTPS with the weight ratios of formamide and HPEP (20/10) and (10/20) at the same original water contents of 10%, stored for 50 days.

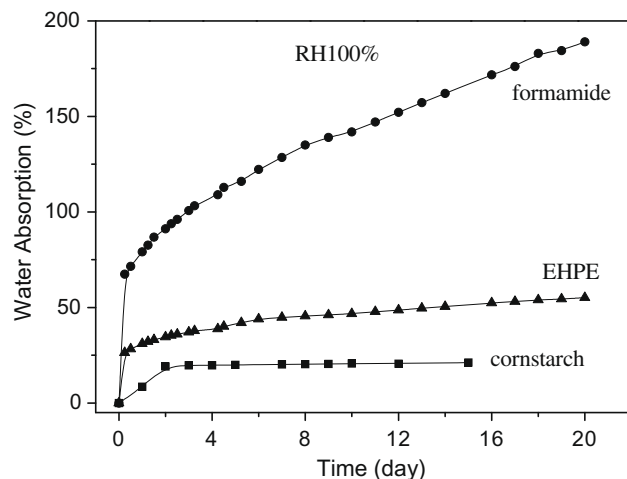


**Fig. 5.** The X-ray diffractograms of FHTPS with the weight ratios of formamide and HPEP (20/10) at the different original water (0% and 15%).

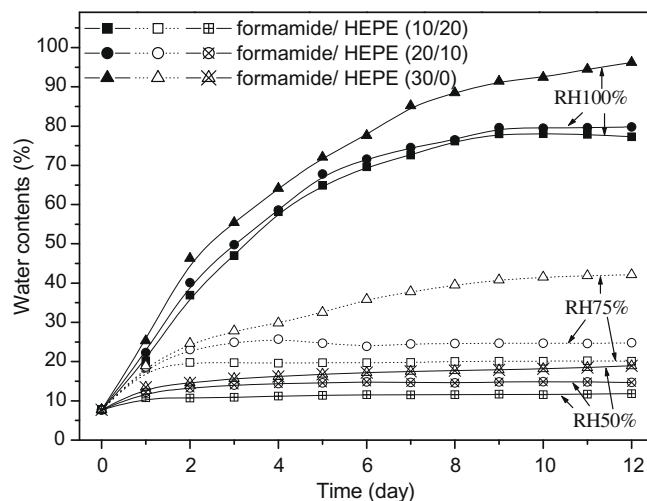
Fig. 7 reveals the effect of the ratios between formamide and HPEP on the water absorption of FHTPS at three RHs. When FHTPS with formamide/HPEP (20/10) and (10/20) are stored at RH 50% and 75% for 12 days, water contents only raise 5% and 15%, respectively. However, they absorb about 70% water contents at 100% for 12 days. FHTPS are still sensitive to water, but the water sensitivity is less than one of TPS plasticized by formamide. With the increasing of HPEP ratios, the absorbed water contents of FHTPS decrease at three RHs. It indicates that the water resistance of TPS is improved by introducing HPEP, because HPEP has a better water resistance than formamide, as shown in Fig. 6.

### 3.5. Mechanical properties

FHTPS with different weight ratios of formamide and HPEP are conditioned at different RHs. Changes in the environmental humid-



**Fig. 6.** The water absorption curve of native corn starch, EHPE and formamide at RH 100%.



**Fig. 7.** The water absorption curves of FHTPS at the different RHs (50%, 75% and 100%).

ity and storage time greatly affect the water contents of FHTPS, which, in turn, induce large changes in the tensile strength and elongation at break (as shown in Fig. 8). When water contents reach above 10%, FHTPS gradually lost mechanical strength with the increasing of water contents. The greater HPEP ratios are, the more the tensile strength of FHTPS is for almost the whole range of water contents. This evolution can be linked to the residual granular structure in the continuous phase, as shown in Fig. 3. The residual granules can act as the reinforced filler in the matrix. The reinforcement effect is more obvious with the increasing of HPEP ratios at the same water contents. However, this reinforcement effect is gradually weakened with the increase of water content; because water can separately form hydrogen bond with the matrix and the filler, and then substitutes original interaction between them.

The elongations at break of FHTPS with different weight ratios of formamide and HPEP change with increasing water contents similarly (Fig. 8) i.e., the elongations of all samples decrease when the water contents deviate from a certain value (about 18%). The more HPEP ratios are, the less the change of the curve is. With the increasing of HPEP ratios, TPS basically has the reducing elongation over the whole range of water contents.

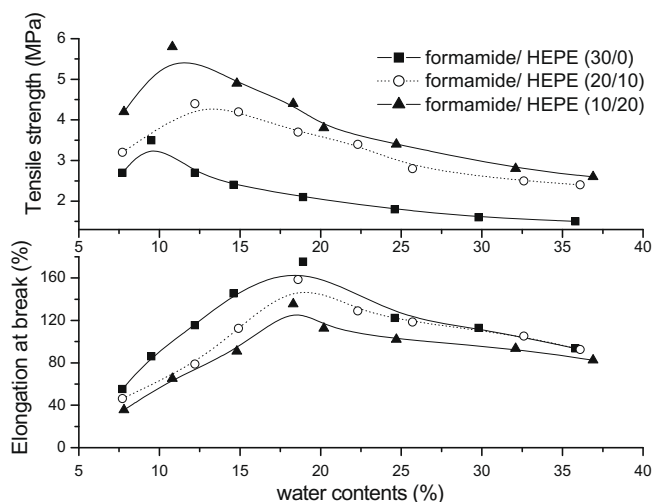


Fig. 8. The effect of water contents on mechanical properties of FHTPS with different weight ratios of formamide and HPEP.

#### 4. Conclusion

The mixture of HPEP and formamide is proved to be as a novel and good plasticizer for starch. HPEP and formamide have the similar intensity of hydrogen-bond formation with starch molecules. As a good solvent for HPEP, formamide and original water can dissolve it, and ensure HPEP to diffuse into the granules of starch before melt extrusion processing. FHTPS composed of 20% formamide, 10% HPEP and 10% original water exhibits the continuous phase without residual granular structure. In views of the crystallinity of FHTPS, the ratio of formamide and HPEP is more important than the original water contents in native starch. Since HPEP has a better water resistance than formamide, the introduction of HPEP can improve water resistance of TPS. With the increasing of HPEP ratios, the tensile strength of FHTPS is increased while the elongation is decreased at the whole range of water contents. At the water contents about 18%, the elongations of FHTPS with different ratios of formamide and HPEP

reach the maximum, while the tensile strengths reach the maximum at the water contents about 10–12%.

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