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Preparation and properties of starch-based film using N-(1-hydroxy-2-methylpropan-2-yl)formamide as a new plasticizer

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ABSTRACT

N-(1-hydroxy-2-methylpropan-2-yl)formamide (HMF) was used as a new plasticizer for corn starch to prepare starch-based film (SF). By scanning electron microscopy (SEM), starch granules were completely disrupted and proved to transfer to homogeneous material. The crystallinity of corn starch and HMF-plasticized starch-based film (HSF) was characterized by X-ray diffraction (XRD). The glass transition temperatures (Tg) of glycerol-plasticized starch-based film (GSF) and HSF were investigated by differential scanning calorimetry (DSC). At relative humidity (RH) 75%, the water resistance of HSF was superior to that of GSF, under the same conditions, water vapor absorption of glycerol was higher than that of HMF. The water vapor permeability of HSF was lower than that of GSF, i.e. the water vapor barrier property of HSF was better than that of GSF. The elongation at break of HSF was higher than that of GSF, but the tensile strength of HSF was inferior to GSF at 75% RH.

KEYWORDS

N-(1-hydroxy-2-methylpropan-2-yl) formamide;
New plasticizer;
Starch-based film;
Water vapor permeability;
Tensile strength.

INTRODUCTION

As nondegradable traditional plastics are widely used, increasing pollution of environment has given rise to concerns about the white pollution, and raises the question how to replace them with natural polymers, being biodegradable and renewable resources. The development and production of biodegradable material made from starch is important to reduce the total amount of plastic waste[1,2]. Therefore, over the past few years, there has been a renewed interest in film made from renewable and natural polymers starch[3,4]. Native starch commonly has a form of granules with about 15-45% crystallinity, and the original starch was composed of amylose and amylopectin[5]. At the same time, starch is an inexpensive, abundant and edible natural resource[6].

In order to modify the properties of starch-based film (SF), plasticizers have to be incorporated, because they can form hydrogen bonds with starch, replacing the strong intra and intermolecular hydrogen bonds in starch[7]. Accordingly, the mechanical properties of starch film can be modified by the addition of plasticizers in minor amounts. During the process, the intra and intermolecular hydrogen bonds in starch are replaced by ones between starch and plasticizers, thus increase the flexibility of the film, and the glass transition temperature decreases. Plasticizers cause significant changes in the barrier properties of starch-based film[1,8]. Starch-based film was prepared using the plasticizers. The traditional plasticizers were polyols such as glycerol[9], which had poor water resistance and were sensitive to the vapor. Meanwhile, amides such as urea[10] can be used as the plasticizers for starch-based film, too. However, urea-plasticized starch-based film stored for a long time, crystallization would occur and the mechanical properties would become worse. So, the properties of SF do not meet what people expect. The type of plasticizer influences the properties of SF. In views of the application and development of SF, it is very important to prepare a new nontoxic plasticizer, which is used to produce SF with desirable properties. In theory, the preparation of new plasticizers is also necessary to study the relationship of plasticizer structure and film properties[11].

N-(1-hydroxy-2-methylpropan-2-yl)formamide (HMF) is one of hydroxyalkylformamides that serve as physiologically harmless humidifiers for cosmetics[12] or for the impregnation of tire-cord made from nylon[13]. It is not reported that HMF is used as plasticizer for starch film.

In this paper, HMF is used to prepare HMF-plasticized starch film (HSF) for obtaining SF with good barrier properties. Glycerol is commonly used as a plasticizer of SF. Here, GSF is regarded as the contrast. This work is focused on processing and characterization of HSF in terms of morphology, XRD, DSC, water vapor absorption, water vapor permeability and mechanical properties.

EXPERIMENTAL

Materials

Corn starch (10.95% moisture) was obtained from the Zhuolu Starch Company (Zhuolu, Hebei, China). Glycerol, methanol and methyl formate (analytical grade) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. (Tianjin, China). 2-amino-2-methyl-1-propanol was purchased from Beijing HWRK Chem Co.,Ltd. (Beijing, China).

Synthesis of N-(1-hydroxy-2-methylpropan-2-yl) formamide (HMF)

N-(1-hydroxy-2-methylpropan-2-yl) formamide (HMF) was synthesized by the reaction of methyl formate and 2-amino-2-methyl-1-propanol according to the reference[14].

The melting point of the product was examined by micro melting point apparatus SGWX-4 (Shanghai, China), it is 68 °C, HMF was confirmed by comparing its melting point with data reported in literature[14].

Starch-based film preparation

Starch-based films were obtained by the casting method. Starch and plasticizer were first mixed. The mixture contained 10 g of starch/100 g of water, and the mass ratios of plasticizer to corn starch were 30:100, 35:100 and 40:100, respectively. The film-forming suspension was heated with continuous stirring and kept at 90°C for 30 min. The film-forming solution was casted on a polystyrene plate. Starch-based films were obtained by evaporating water in an oven at 50 °C.

Scanning electron microscopy (SEM)

Corn starch was investigated with the scanning electron microscope Phillips XL-3 (FEI Company, Hillsboro, USA), operating at an acceleration voltage of 20 kV. Starch powders were suspended in acetone. The suspension drops were drawn on the glass slide, dried for removing the acetone, and then vacuum-coated with gold for SEM.

An S-4800 scanning electron microscope (HITACHI Company, Tokyo, Japan) was used to examine the morphology of fractured surfaces of SF, operating at an acceleration voltage of 5 kV. The conditioned SF samples were cryo-fractured in liquid nitrogen. The fracture faces were vacuum-coated with platinum for SEM.

X-ray diffraction (XRD)

The SF sample was 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° (2θ) at the ambient temperature by an Empyrean diffractometer (Netherlands) operated at the Cu/Kα radiation.

Differential scanning calorimetry (DSC) testing

The DSC was used to investigate the crystallization and melting behavior of the prepared SF[15]. To simulate the conditions during application, GSF and HSF were exposed to air (relative humidity around 50%) before DSC measurements. The water contents of GSF and HSF containing 30% plasticizer were 16.38% and 9.72%, respectively. DSC measurements were carried out in a PerkinElmer DSC 4000 (PerkinElmer, USA). The DSC was calibrated with pure indium. An empty pan was used as reference. Samples of GSF and HSF were scanned at a heating rate of 20°C/min in a sealed pan. Glass transition temperatures were determined from the resulting thermograms observed during heating by the Pyris software and identified as second-order transitions[16].

Water vapor absorption

Measurement of water contents of GSF, HSF and plasticizers.

The original water contents (dry basis) of SF were determined gravimetrically by drying small pieces of SF at 105°C for 12h. At this condition, evaporation of the plasticizers was negligible[17]. The original water content (k) of starch film was calculated as follows:

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

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

Glycerol and HMF were stored in a closed container in the presence of a saturated NaCl solution (providing relative humidity (RH) 75%)[18] at 20°C and weighed. According to the Eq. (1) above-mentioned, the water content of plasticizer was calculated. w_2 and w_1 were the mass of plasticizer containing water and pure plasticizer, respectively. The data were carried out in triplicate.

Measurement of water contents of bars of GSF and HSF stored at 75% RH for a period.

The pieces of GSF and HSF containing 35% plasticizers were stored in closed containers in the presence of saturated NaCl solution (providing RH 75%) at 20°C. The samples were weighed every day. The water contents of GSF and HSF were calculated on the base of mass of dried GSF and HSF. The data were averages of 3 specimens.

Water vapor permeability (WVP)

For the WVP studies, the starch-based films were cut to a suitable size and fixed onto cylindrical bottle containing granular anhydrous $CaCl_2$. The thickness of each film was measured with a micrometer at three randomly selected points before the film was attached to the bottle. The bottle was placed in a desiccator at 75% RH, resulting in relative vapor pressures gradient of 0/75% across the film at 20°C. The WVP (National standard of China GB1037-88) was determined gravimetrically as a function of time for 7 days. The bottle was shaken horizontally after every weighing. WVP ($\mathrm{g\ m^{-1}\ s^{-1}\ Pa^{-1}}$) was calculated with Eq. (2), where Δm was the weight of the water permeated through the film, d was the thickness of the film, A was the permeation area of the film, t was the time of permeation and Δp was the water vapor pressure difference between both sides of the film. The tests were averages of 3 specimens.

$$WVP = \frac{\Delta m \cdot d}{A \cdot t \cdot \Delta p} \quad (2)$$

Mechanical testing

The starch-based films were cut into strips and stored in closed chamber at 75% RH for 48 hours. Mechanical testing (National Standard of China GB1040-79) of samples was determined in the TH-5000 Materials Testing Machine (Jiangsu, China) at a speed of 10 mm/min. The data were averages of 3 specimens.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM)

The morphology of starch and the SF was shown in Figure 1.

Compared with starch granules (Figure 1a), the morphology of GSF and HSF were present in the homogeneous material (Figure 1) for the GSF containing 30% weight content of glycerol (Figure 1b) and the HSF containing 30% weight content of HMF (Figure 1c). According to the gelatinization mechanism, starch granules swollen and broken into pieces with releasing amylose and amylopectin molecules into solution during heat treatment of starch dispersion. Figure 1 showed that there was no starch granules and remnant presenting in the film at the presence of HMF. This meant the starch polymer was plasticized completely. SEM ob-

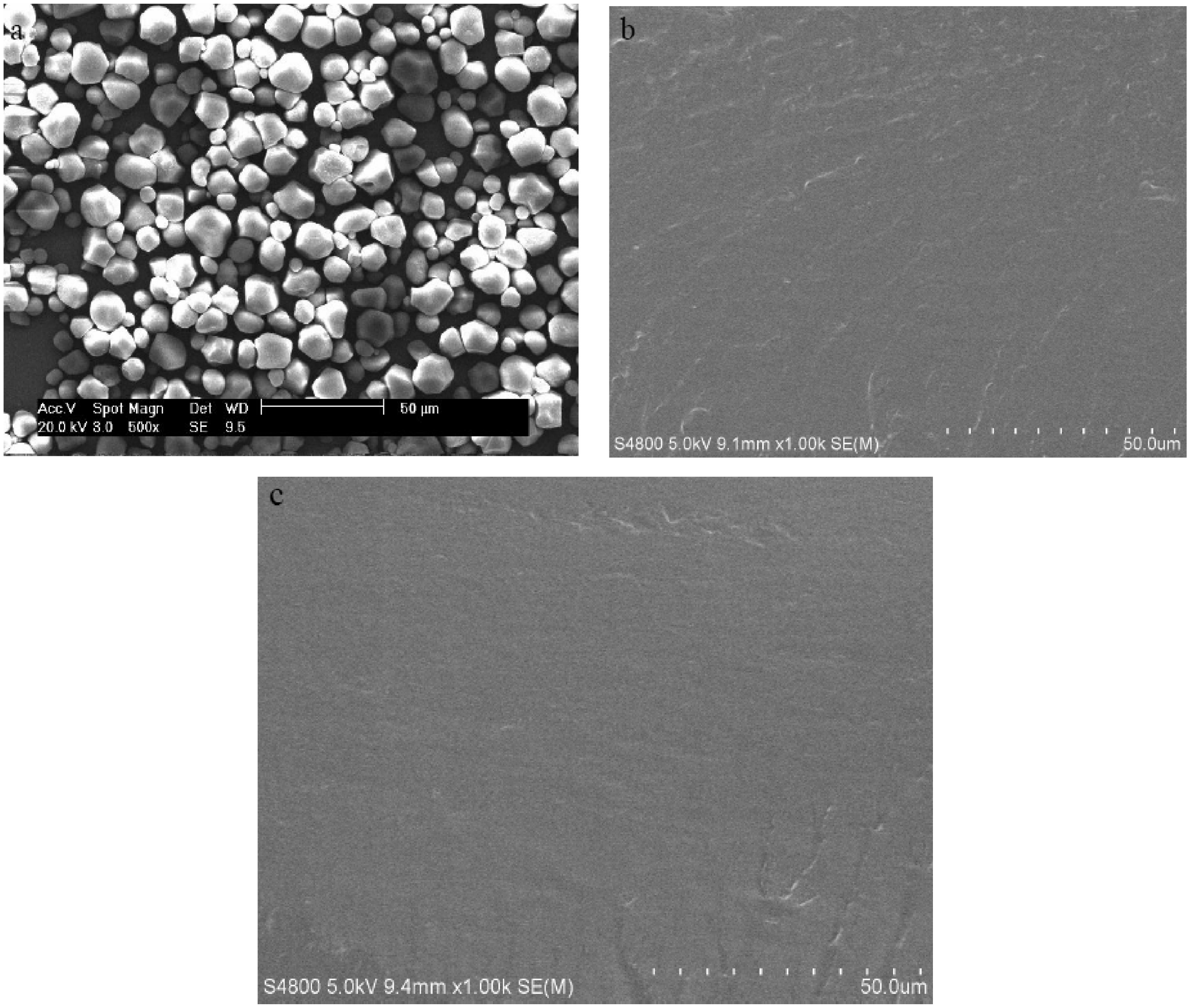

Figure 1 : SEM micrograph of (a) corn starch, (b) GSF containing 30% glycerol, (c) HSF containing 30% HMF

servations of films with different plasticizer (glycerol and HMF) did not show structural differences.

X-ray diffraction analysis (XRD)

The X-ray diffraction patterns of corn starch, GSF and HSF were shown in Figure 2. Corn starch had an A-type crystalline pattern (Figure 2, line a). Compared with starch, the crystal structure of GSF and HSF changed. During the gelatinization of the starch granules, A-type crystallinity of corn starch disappeared. Starch-based films could have an amorphous character, because the thermal treatment of film-forming suspension provoked starch gelatinization, causing disruption of the double helix conformations of corn starch, however, the plasticizer glycerol or HMF in the films may have increased the macromolecular mobility, allowing the formation of microcrystalline junctions, i.e. some some re-crystallization occurred[19]. Other crystallinity was formed in GSF (Figure 2, line b) and HSF

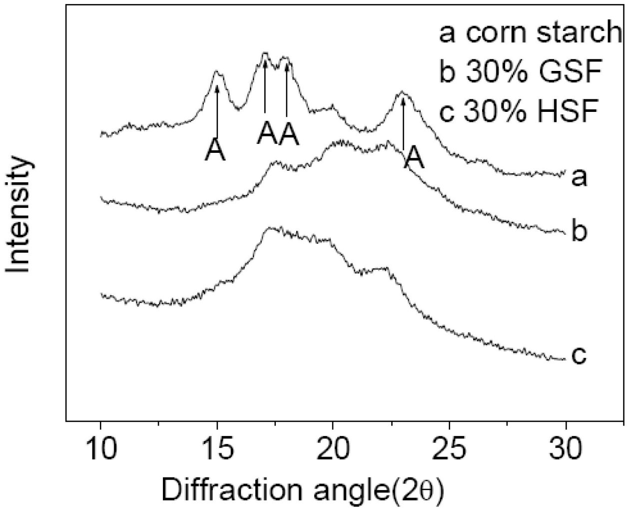

Figure 2 : Diffractograms of corn starch, GSF and HSF

(Figure 2, line c)[20].

DSC analysis

The DSC measurements served to determine the relaxational transitions of the SF. As shown in Figure 3, the transitions of SF could be linked to their glass transitions[16]. The Tg of HSF containing 30% HMF was 8.45°C, which was less than that of GSF (11.55°C) containing 30% plasticizer. This evolution could be ascribed to the strong interactions between the starch and plasticizer. In the views of Tg, as the plasticizer, HMF could form stronger interaction with starch than glycerol.

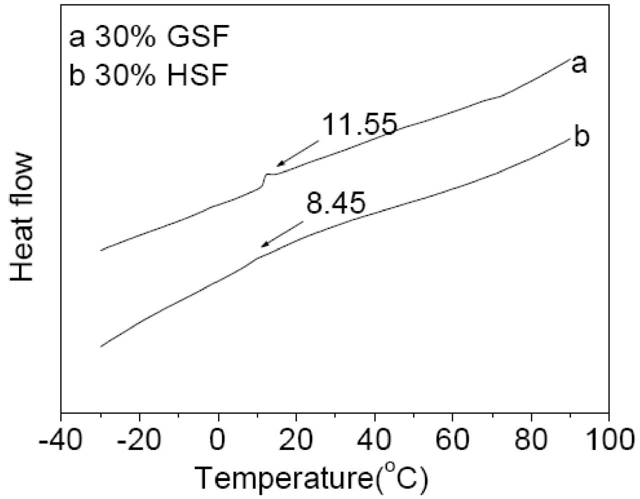

Figure 3 : DSC thermograms of GSF and HSF

Water vapor absorption

The mechanical properties of SF were sensitive to humidity, so the water contents of HSF were examined, the GSF was a contrast.

As shown in Figure 4a, at 75% RH, the equilibrium water content of GSF (containing 35% glycerol) was higher than that of HSF (containing 35% HMF). So the water resistance of HSF was superior to that of GSF.

The hydrophilicity of plasticizer was related to water resistance of starch film. As shown in Figure 4b, under the same conditions, water vapor absorption of glycerol was higher than that of HMF, so glycerol was more hydrophilic than HMF.

Water vapor permeability

As shown in Figure 5, The WVP of HSF was lower than that of GSF. For example, the WVP of HSF containing 30% HMF was 1.13×10^{-13} gm^{-1} s^{-1} Pa^{-1}, while the WVP of GSF containing 30% glycerol was 3.87×10^{-13} gm^{-1} s^{-1} Pa^{-1}. Therefore, the water vapor barriers of HSF were superior to that of GSF.

Generally, the hydrophilicity of plasticizer was related to WVP of SF. As shown in Figure 4b, under the same conditions, water vapor absorption of glycerol was higher than that of HMF, so glycerol was more hydrophilic than HMF. GSF was more hydrophilic than HSF. At the same experimental conditions, GSF absorbed more water molecules than HSF. $CaCl_2$ was far more hydrophilic than both GSF and HSF. At the present of $CaCl_2$, GSF containing more water lost more water to $CaCl_2$ compared with HSF. So the WVP of GSF was higher than that of HSF.

Mechanical properties

After HSF stored at 75% RH for 2 days, tensile

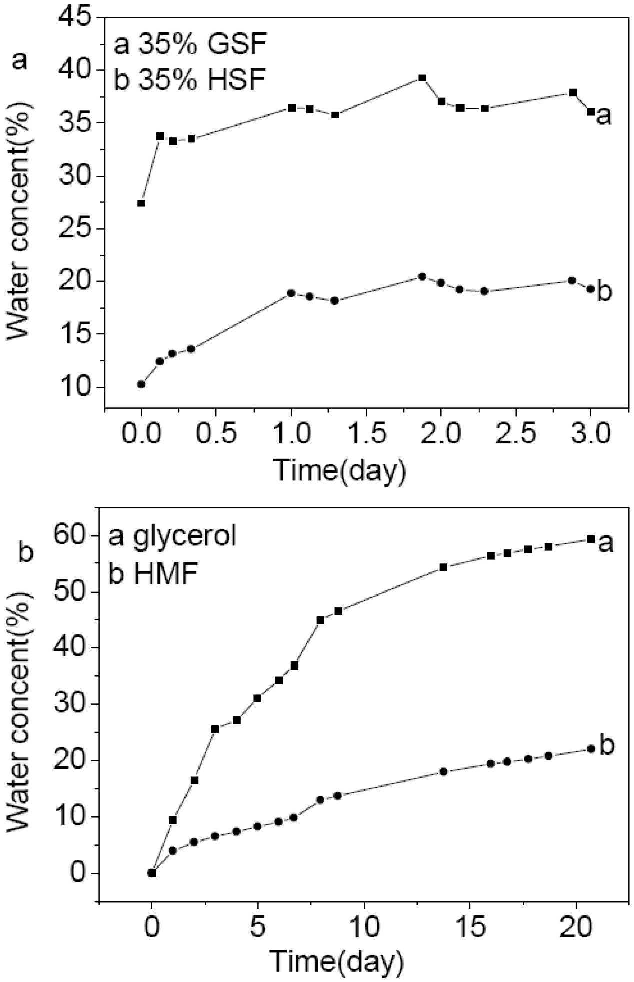

Figure 4 : (a) Water contents of GSF and HSF containing 35% plasticizer as function of storage time at 75% RH. (b)Water contents of glycerol and HMF as function of storage time at 75% RH

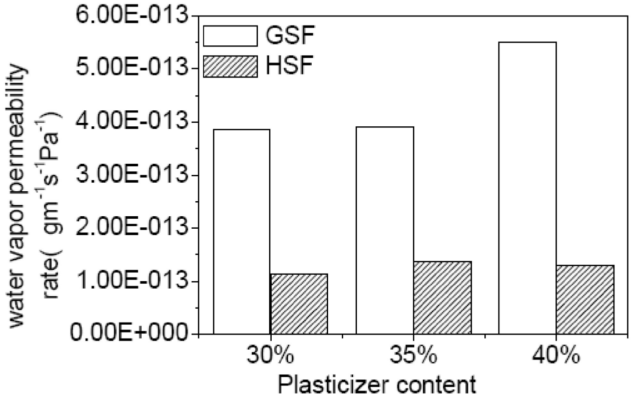

Figure 5 : Water vapor permeability of GSF and HSF

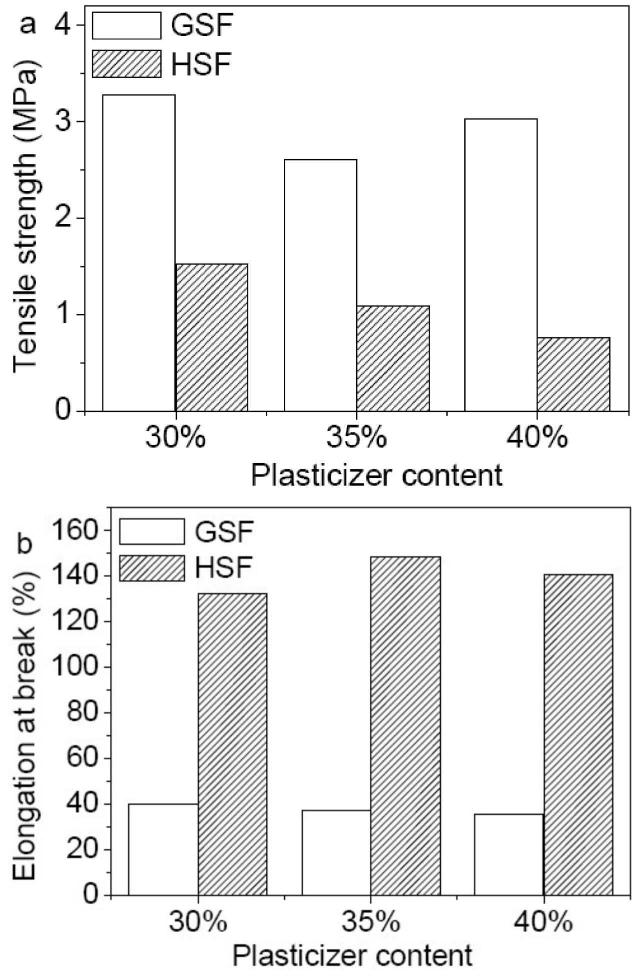

Figure 6 : (a) Tensile strengths and (b) Elongations at break of GSF and HSF stored at 75% RH for 2 days

strength and elongation at break of HSF were tested. In order to introduce the mechanical properties of HSF clearly, GSF was chosen as the contrast.

As shown in Figure 6, when starch film containing 35% plasticizer was stored at RH 75% for 2 days, the tensile strength and the elongation at break were 2.60 MPa and 37.5% for GSF. At the same time, the ones were 1.09 MPa and 148.3% for HSF. At the same percentage of plasticizer contents, the elongation at break of HSF was higher than that of GSF, while the tensile strength was inferior to GSF. Therefore, HSF was more flexible than GSF.

With increasing HMF content, the tensile strength of HSF decreased, whereas the elongation at break increased generally. For example, after HSF was stored at RH 75% for 2 days, the tensile strengths of HSF containing 30%, 35%, 40% of plasticizer were 1.52, 1.09, 0.76 MPa, respectively. The elongations at break of HSF containing 30%, 35%, 40% plasticizer were 132.2%, 148.3%, 140.9% respectively. HMF acted as a dilutor, formed stronger hydrogen bond interactions with starch and weaken the interaction of the molecules. Thus, the tensile strength decreased. At the same time, it also acted as a plasticizer that improved the movement of the segments and macromolecules, which led to the increase of the elongation at break.

CONCLUSIONS

HMF was proven to be effective as a new plasticizer for corn starch. From the analysis of SEM, starch granules were completely disrupted and transferred to homogeneous material. X-ray diffraction analysis indicated A-type crystallinity of corn starch disappeared and other crystallinity was formed. Analysis of DSC showed that Tg of HSF was lower than that of GSF. The water resistance of HSF was superior to that of GSF. WVP of HSF was less than that of GSF, i.e. the water vapor barrier property of HSF is better than that of GSF. At RH 75%, the elongation at break of HSF was higher than that of GSF, but the tensile strength of HSF was inferior to that of GSF.

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