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Preparation and properties of starch-based film using *N*,*N*-bis(2-hydroxyethyl)formamide as a new plasticizer

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ABSTRACT

N,*N*-Bis(2-hydroxyethyl)formamide (BHF) was synthesized efficiently and used as a new plasticizer for corn starch to prepare flexible starch film. The hydrogen bond interaction between BHF and starch was proven by Fourier-transform infrared (FT-IR) spectroscopy. By scanning electron microscope (SEM), starch granules were completely disrupted and a continuous phase was obtained. The crystallinity of corn starch and BHF-plasticized starch film (BSF) was characterized by X-ray diffraction (XRD). The water resistance of BSF was better than that of glycerol-plasticized starch film (GSF). Water vapor permeability of BSF was lower than that of GSF. Tensile strengths of BSF were inferior to those of GSF, while the elongations at break of BSF were higher than those of GSF.

1. Introduction

Over the past few years, there has been a renewed interest in film made from renewable and natural polymers such as starch (Mali, Grossmann, Garcia, Martino, & Zaritzky, 2002; Mathew & Abraham, 2008). Several studies have analyzed the properties of starch-based films. Edible or biodegradable films are not meant to totally replace synthetic packaging films; however, they do have the potential to replace the conventional packaging in some applications. Starch is quite cheap, abundant, biodegradable, and edible (Alves, Mali, Beleia, & Grossmann, 2007). Starch is polysaccharide composed of amylose, a linear or sparsely branched polymer, and amylopectin, a highly branched polymer.

The properties of starch film can be modified by the addition of various chemicals in minor amounts. For example, plasticizers, such as glycerol and sorbitol are often used to modify the mechanical properties of the film. These compounds decrease intermolecular attractions between adjacent polymeric chains, thus increasing film flexibility. Incorporation of these additives may, however, cause significant changes in the barrier properties of the film (Rodriguez, Oses, Ziani, & Mate, 2006).

In most literature for starch film, polyols as plasticizers usually are used such as glycerol, sorbitol, ethylene glycol (Lourdin, Coignard, Bizot, & Colonna, 1997). Urea can be used as plasticizer for starch film (Lourdin et al., 1997). However, the properties of starch film do not reach what people expect. The type of plasticizer influences the properties of films. In views of the application and development of starch film, it is very important to prepare a low cost and nontoxic plasticizer, which is used to produce film with desirable properties. In basic research, the preparation of new plasticizers is also necessary to study the relationship of plasticizers structure and film properties (Tarvainen, Sutinen, Somppi, Paronen, & Poso, 2001).

N,*N*-Bis(2-hydroxyethyl)formamide (BHF) is one of hydroxyalkylformamides that serve as physiologically harmless humidifiers for cosmetics (Coupland & Smith, 1986) or for the impregnation of tire-cord made from nylon (Kibler & Richard, 1973). Many synthetic methods for preparation of BHF have been reported. However, some of these methods have drawbacks such as high pressure (Ricci, Sbrana, & Braca, 1991), and use of much methanol as solvent (Frings & Grahe, 1992).

In this paper, an efficient and practical method is used to synthesize BHF without any solvent. As a new plasticizer, BHF is used to prepare BHF-plasticized starch film (BSF). Glycerol is commonly used as a plasticizer of starch film. Here glycerol-plasticized starch film (GSF) is regarded as the contrast. This work is focused on processing and characterization of BSF in terms of FT-IR, morphology, XRD, water vapor absorption, water vapor permeability and mechanical properties.

2. Experimental

2.1. Materials

Corn starch (7.62% moisture) was obtained from the Langfang Starch Company (Langfang, Hebei, China). Glycerol,

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diethanolamine and ethyl formate (analytical grade) were purchased from Tianjin Chemical Reagent Ltd. (Tianjin, China).

2.2. Synthesis of N,N-bis(2-hydroxyethyl)formamide

One mole diethanolamine was introduced into a 500 mL flask equipped with a stirrer, a reflux condenser, a dropping funnel and a thermometer, it was cooled to 27 °C in an ice bath and then 1 mol ethyl formate was added during 30 min. The temperature in the flask rose to 30 °C. The reaction mixture was stirred for 1 h at 60 °C by monitoring with thin layer chromatography (TLC). Then the byproduct ethanol evaporated under reduced pressure at 60 °C until ethanol was not distilled from the mixture again. Subsequently the mixture was cooled to 27 °C in an ice bath, followed by addition of 0.05 mol 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 until ethanol was not distilled from the mixture again. The residue was cooled to 27 °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, heated under reduced pressure at 110 °C until the mass of the liquid was constant. A viscous liquid was gotten. The purity was 97% according to the column chromatography on neutral aluminum oxide (200–300 mesh) eluted with mixture of dichloromethane and methanol. The yield of BHF was 97%. The product was confirmed by ^{1}H NMR, IR, MS. The chemical reaction equation was shown in Fig. 1.

^{1}H NMR spectra were measured on a VARIAN INOVA 500 MHz spectrometer using TMS as internal standard and CD_3SOCD_3 as solvent. The IR spectra were recorded with a BIO-RAD FTS3000 IR spectrometer (KBr). Mass spectra were determined on an LCQ Advantage MAX spectrometer (ESI).Data for *N*,*N*-bis(2-hydroxyethyl)formamide:$\nu_{\max}$ (KBr): 3461–3332 (OH), 2943 ($-CH_2-$), 2886 ($-CH_2-$), 1659 (C=O) cm^{-1}; ^{1}H NMR (CD_3SOCD_3, δ ppm): 7.950 (s, 1H, HCON), 4.738 (t, 1H, *J* = 5.5 Hz, –OH), 4.701 (t, 1H, *J* = 5.5 Hz, –OH), 3.475–3.439 (m, 4H, $-CH_2O-$), 3.305–3.264 (m, 4H, $-CH_2N$); m/z (%): 134 (MH$^+$, 100), 156 (MNa$^+$, 8.1).

2.3. Starch film preparation

Films were obtained by the casting method. Starch and plasticizer were first mixed and dispersed in water. The mixture contained 5 g of starch/100 g of water and 25, 30, 35 g of plasticizer/100 g of starch. The film-forming suspension was heated with continuous stirring and kept at 85 °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.

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

The IR spectra were measured with a BIO-RAD FTS3000 IR Spectrum Scanner (Hercules, CA, USA). The starch films were measured in reflection mode.

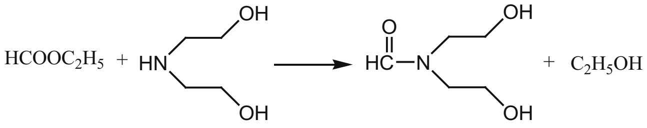

Fig. 1. Chemical reaction equation of synthesizing *N*,*N*-bis(2-hydroxyethyl)formamide.

2.5. Scanning electron microscopy (SEM)

Corn starch and the fracture surfaces of the BSF samples were investigated with the scanning electron microscope Phillips XL-3 (FEI Company, Hillsboro, OR, 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. The conditioned BSF samples were cryo-fractured in liquid nitrogen. The fracture faces were vacuum-coated with gold for SEM.

2.6. X-ray diffraction (XRD)

The starch films 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° (2θ) at the ambient temperature by a Rigaku D diffractometer (Japan) operated at the Cu/Kα radiation.

2.7. Water vapor absorption

Measurement of water contents of new GSF, BSF and plasticizers.

The pieces of films were cut into small pieces and the pieces weighed immediately. They were then dried in an oven at 105 °C overnight and weighted. The original water content (k) of starch film was calculated as follows:

$$k = \frac{w_2 - w_1}{w_1} \times 100\% \tag{1}$$

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

Glycerol and BHF were stored in a closed container in the presence of distilled water (providing relative humidity (RH) 100%) 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 averages of 3 specimens.

Measurement of water contents of bars of GSF and BSF stored at different relative humidities (RHs) for a period.

The pieces of GSF and BSF were stored in closed containers in the presence of different compounds, namely, a saturated $MgCl_2$ solution, a saturated K_2CO_3 solution, a 35.64% $CaCl_2$ solution, a saturated $CuCl_2$ solution, a saturated NaCl solution and a saturated $(NH_4)_2SO_4$ solution (providing RHs of 33%, 44%, 50%, 68%, 75 and 80%, respectively) at 20 °C (Godbillot, Dole, Joly, Rogé, & Mathlouthi, 2006; Ma & Yu, 2004). The samples were weighed every day. Equilibrium was reached when three consecutive daily weighing were constant (±1 mg/day) (Quirijins, van Boxtel, van Loon, & van Straten, 2005; Raj, Raj, Madan, & Siddaramaiah, 2003). The water contents of GSF and BSF at different RHs were calculated on the base of mass of dried GSF and BSF. The data were averages of 3 specimens. Equilibrium formulae of water vapor absorption of GSF and BSF were obtained by fitting the data in Origin 6.1 software.

2.8. Water vapor permeability (WVP)

Granular anhydrous $CaCl_2$ was used as a desiccant in a cylindrical bowl that was covered with the studied films attached with tape to the bowel. The distance between the surface of the desiccant and the film was about 3 mm, as suggested by National standard of China GB1037-88. The thickness of each film was measured with a micrometer (accuracy of 0.01 mm) at six randomly selected points before the film was attached to the bowel. The bowel was placed in a disiccator at a RH of 75%, resulting in relative vapor pressures gradient of 0/75% across the film at 20 °C. The progress of water vapor permeation was determined gravimetrically as a function of time for 7 days. The bowl was shaken horizontally after every weighing. WVP (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. WVP was given in SI units. The tests were carried out in triplicate.

$$\mathrm{WVP} = \frac{\Delta m \cdot d}{A \cdot t \cdot \Delta p} \tag{2}$$

2.9. Mechanical testing

Mechanical testing (National standard of China GB1040-79) of samples was determined in the AX M350-10KN Materials Testing Machine (Testometric, Rochdate, UK) at a crosshead speed of 10 mm/min. The data were averages of 5 specimens.

3. Results and discussion

3.1. FT-IR analysis

The wavenumber shift of stretching vibrations of corn starch could be observed in Fig. 2 (corn starch and BSF). The peak wavenumber 1157 cm^{-1} was ascribed to the C–O bond stretching of the C–O–H group in starch. The characteristic peaks at 1082 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 wavenumber 3396 cm^{-1} was attributed to starch O–H bond stretching. In BSF, all the peaks shifted to lower wavenumbers, for example, the peaks 1157 and 1082 cm^{-1} in starch shifted to 1150 cm^{-1} and around 1076 cm^{-1} in BSF, respectively.

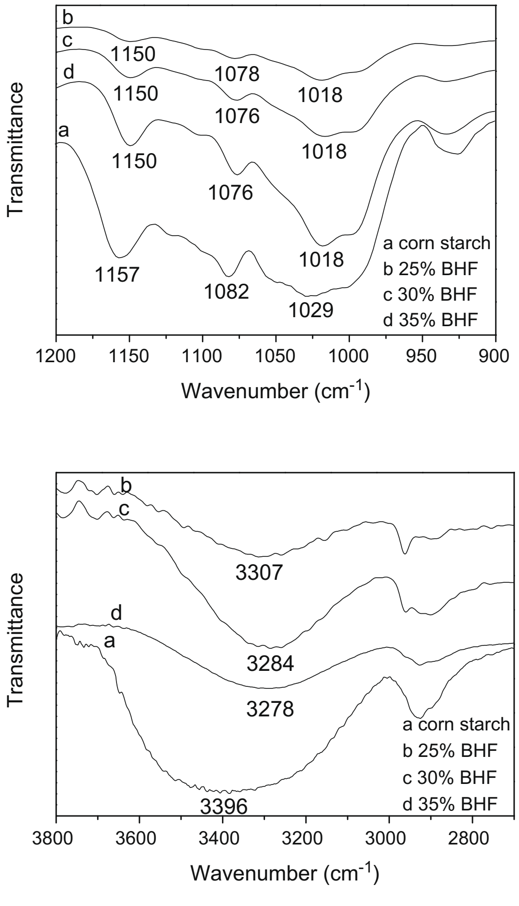

Fig. 2. FT-IR spectra of corn starch and BSF.

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 are directly related to the wavenumber shift of the stretching bands of functional groups in starch. The lower the peak wavenumber is, the stronger the interaction is (Pawlak & Mucha, 2003). All these results indicated that stronger hydrogen bonds were formed between BHF and starch compared with intra- and intermolecular hydrogen bonds in starch. FT-IR spectra had been analyzed, because of the groups –O–H and –CO–N in BHF, stable hydrogen bonds were formed between BHF and starch, which could weaken the intra- and intermolecular hydrogen bonds in starch.

3.2. Scanning electron microscopy (SEM)

The morphology of starch and the BSF was shown in Fig. 3. Compared with starch granules, BSF formed a continuous phase. 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. Fig. 3 showed that there was no starch granules and remnant presenting in the film at the present of BHF. This meant the starch polymer was solubilized completely.

During the gelatinization of the starch granules, amylose and amylopectin molecules released into the solution. According to Liu and Han (2005), without plasticizers, amylose and amylopectin would form a film with a biphasic structure, which had an amylose-rich phase and an amylopectin-rich phase. The network of amylose-rich clusters was embedded in the amylopectin-rich amorphous background. The interactions between the amylose and amylopectin molecules contributed to the film formation, but were so strong that the starch films were readily brittle and rigid. According to the analysis of FT-IR above-mentioned, the plasticizers in the starch films could form hydrogen bonds with starch molecules, which weakened the strong action of starch intermolecular and intramolecular hydrogen bonds, and then reduce the interaction between amylose and amylopectin molecules making the starch film flexible. No pores or cracks were detected by SEM observations. SEM observations of films with different plasticizer contents did not show structural differences.

3.3. X-ray diffraction analysis (XRD)

The X-ray diffraction patterns of corn starch and BSF exposed to the air (The RH was around 50%) for 7 days were shown in Fig. 4. Compared with starch, the crystal structure of BSF changed. During the gelatinization of the starch granules, A-type crystallinity of corn starch (Fig. 4, line a) disappeared. According to Bergo et al. (2008), starch 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 BHF in the films may have increased the macromolecular mobility, allowing the formation of microcrystalline junctions, i.e. some re-crystallization occurred. $\mathrm{V_H}$-type crystallinity was formed (Fig. 4, line c) (van Soest, Hulleman, de Wit, & Vliegenthart, 1996).

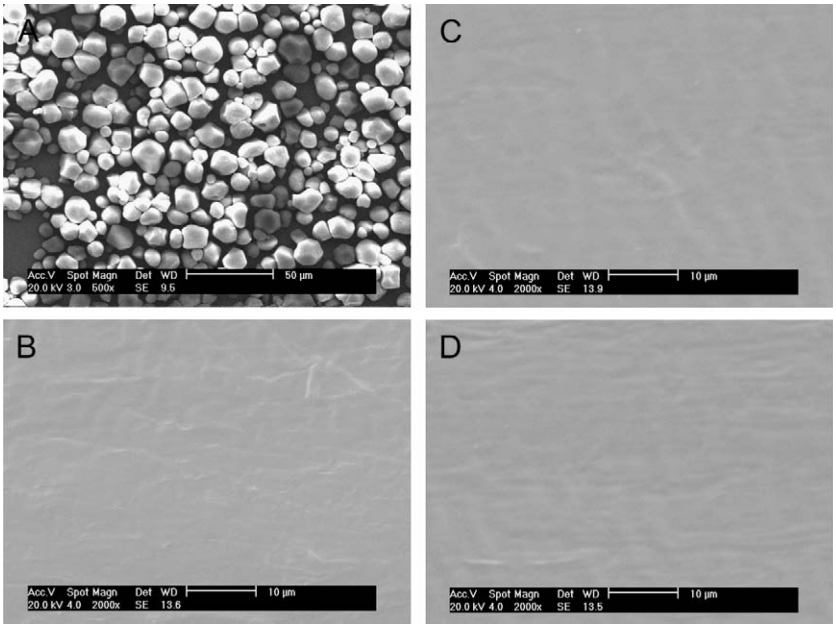

Fig. 3. SEM micrograph of (A) corn starch, (B) BSF containing 25% BHF, (C) BSF containing 30% BHF, (D) BSF containing 35% BHF.

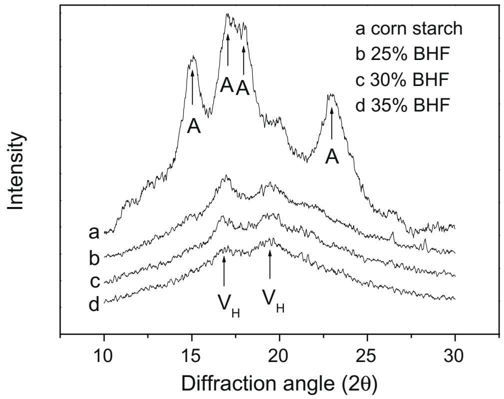

Fig. 4. Diffractograms of corn starch and BSF exposed to the air for 7 days.

3.4. Water vapor absorption

Starch film was sensitive to humidity, the influence of which on the properties of starch film was important. BET and GAB model were usually used to describe the water vapor absorption isotherms. Peleg defined a new sorption isotherm model based on four parameters: $M = k_1\left(\frac{p}{p_0}\right)^{n_1} + k_2\left(\frac{p}{p_0}\right)^{n_2}$, k_1, n_1, k_2, n_2 were constants. Although the parameters used in the Peleg model did not have fundamental meaning, it was a precise model to predict sorption isotherms, due to its four fitting parameters. Therefore, the Peleg model had been successfully applied to many food systems for relative humidity of up to 95%. The Peleg model represented an alternative to the classic BET and GAB models. It could be used to accurately represent sorption isotherms due to the presence of an extra parameter in the equation. The drawback of using this model was the lack of theoretical background in its development, and thus it did little to improve the fundamental understanding of the differences in sorption behavior (Enrion, Hill, & Mitchell, 2007).

In the paper, Peleg model was used to describe the relationship of starch film water content and RH. The parameters for the sorption models for GSF and BSF were shown in Table 1. As shown in Fig. 5, at the same RH, the balance water content of GSF was larger than that of BSF. The highest balance water contents of GSF and BSF stored at RH 68% for 7 days were 19.1%, 20.4%, 21.3% and 14.3%, 14.7%, 15.8% (corresponding to the plasticizer contents 25%, 30%, 35%), respectively. The water resistance of BSF was better than that of GSF. With increasing BHF content, the water resistance of BSF became worse at high RH.

In the opinion, the hydrophilicity of plasticizer was related to water resistance of starch film. As shown in Fig. 5B, under the same conditions, water vapor absorption of glycerol was higher than that of BHF, so glycerol was more hydrophilic than BHF. The water resistance of BSF was better than that of GSF.

3.5. Water vapor permeability

WVP were examined. As shown in Fig. 6, WVP increased as the concentration of plasticizer increased in the range of plasticizer content studied. These results could be related to structural modifications of the starch network produced by the plasticizer and to the hydrophilic character of plasticizer, which favored the absorption and desorption of water molecules. Plasticizers reduced intra- and intermolecular forces in starch. Plasticizers extended, diluted and softened the structure effectively, the starch chain mobility was increased. Plasticizer caused a greater flexibility in polymeric structure, which increased water sorbed mobility within the structure. As a result WVP increased with film plasticizer content (Bertuzzi, Castro Vidaurre, Armada, & Gottifredi, 2007). For example, the WVP of GSF containing 25%, 30%, 35% of plasticizer were 9.18×10^{-12}, 1.62×10^{-11}, 1.93×10^{-11} g m^{-1} s^{-1} Pa^{-1}, respectively.

The WVP of BSF were lower than those of GSF. For example, the WVP of BSF containing 25% BHF was 8.19×10^{-12} g m^{-1} s^{-1} Pa^{-1}, while the WVP of GSF containing 25% glycerol was 9.18×10^{-12} g m^{-1} s^{-1} Pa^{-1}. In the opinion, the hydrophilicity of plasticizer was related to WVP of TPS. As shown in Fig. 5B, under the same conditions, water vapor absorption of glycerol was higher than that of BHF, so glycerol was more hydrophilic than BHF. GSF was more hydrophilic than BSF. At the same experimental conditions, GSF absorbed more water molecules than BSF. $CaCl_2$ was far more hydrophilic than both GSF and BSF. At the present of $CaCl_2$, GSF containing more water lost more water to $CaCl_2$ compared with BSF. So the WVP of GSF was higher than that of BSF.

Table 1
Estimated values of coefficients obtained for Peleg sorption model applied to experimental absorption data for starch film.

Constant	25% glycerol	30% glycerol	35% glycerol	25% BHF	30% BHF	35% BHF
k_1	0.27304	0.30505	0.30716	0.24339	0.2399	0.26306
n_1	1.07335	1.16609	1.04563	1.44902	1.33088	1.36757
k_2	1.46647	3.92872	13.52489	2.09851	1.6765	10.59034
n_2	14.08471	18.30166	23.40733	18.36024	16.84981	24.83634

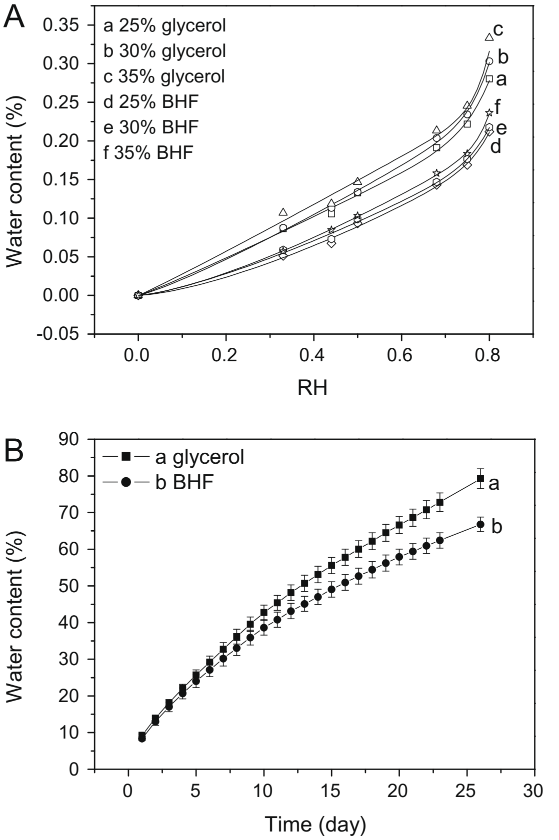

Fig. 5. (A) Water contents of GSF and BSF as function of relative humidities. (B) Water contents of glycerol and BHF as function of storage time at 100% RH.

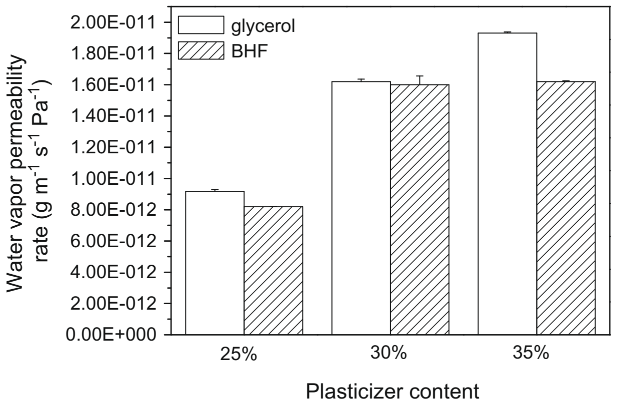

Fig. 6. Water vapor permeability of GSF and BSF.

3.6. Mechanical properties

Tensile strength and elongation at break of TPS stored at 33%, 44%, 50%, 68% RHs, respectively, for 7 days were examined. In order to introduce the mechanical properties of BSF clearly, GSF was chosen as the contrast. Although the tensile strengths of BSF were inferior to those of GSF, the elongations at break of BSF were higher than those of GSF. As shown in Fig. 7, when starch film containing 30% plasticizer was stored at RH 50% for 7 days, the tensile strength and the elongation at break were 4.2 MPa and 34.9% for GSF, and the ones were 1.3 MPa and 107.7% for BSF.

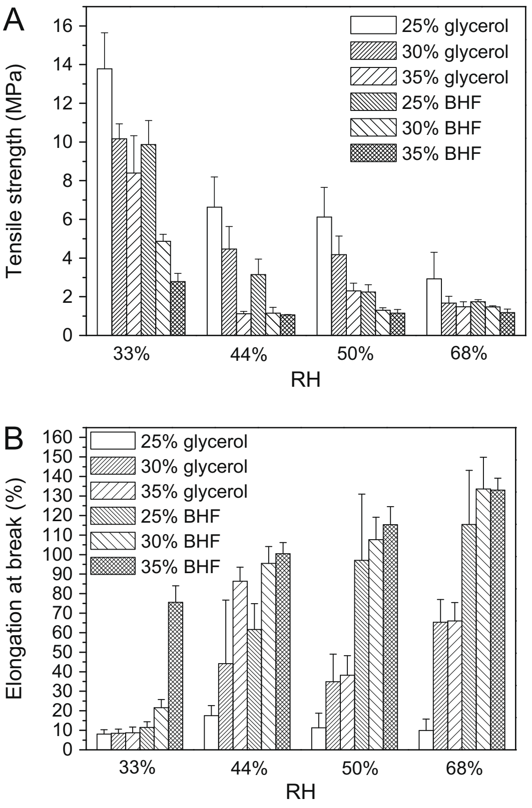

Fig. 7. (A) Tensile strengths and (B) elongations at break of GSF and BSF stored at different RHs for 7 days.

With increasing BHF content, the tensile strength of BSF decreased, whereas the elongation at break increased. For example, after BSF was stored at RH 33% for 7 days, the tensile strengths of BSF containing 25%, 30%, 35% of plasticizer were 9.9, 4.9, 2.8 MPa, respectively. The elongations at break of BSF containing 25%, 30%, 35% plasticizer were 11.5%, 21.6%, 75.6%, respectively. BHF acted as a dilutor and lowered 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.

4. Conclusions

BHF was synthesized by an efficient and practical method and proven to be effective as a new plasticizer for corn starch. BHF 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 a continuous phase was obtained. X-ray diffraction analysis indicated A-type crystallinity of corn starch disappeared and V_H-type crystallinity was formed. BSF was material with better water resistance than GSF. WVP of BSF was lower than that of GSF. The tensile strengths of BSF were inferior to those of GSF, while the elongations at break of BSF were higher than those of GSF.

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