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Preparation and properties of ethylenebisformamide plasticized potato starch (EPTPS)

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Abstract

Ethylenebisformamide plasticized potato starch (EPTPS) was prepared by extrusion. Starch was blended with ethylenebisformamide at 25, 30, and 35% (W/W) and extruded in a single-screw extruder. The samples were extruded at 135–140–135–135 °C from feed zone to die. FT-IR expressed that the microcosmic chemical environments of the group in EPTPS compared to the native potato starch, which indicated that, the strong and stable hydrogen bond had been formed between ethylenebisformamide and starch. By Scanning Electron Microscope (SEM) native potato starch granules were proved to transfer to a continuous phase. After being stored for 1 week at RH = 33%, the mechanical properties of ethylenebisformamide plasticized thermoplastic starch (EPTPS) was also studied and the elongation reached to 140% utmost with a decrease of the tensile strength. X-ray diffraction (XRD) showed that the typical B-style crystallinity in the native potato starch has been destructed. On the other hand, water resistance of EPTPS was better than glycerol plasticized potato starch (GPTPS). It decreased from 50.2% for the glycerol plasticized potato starch down to 35.3% for the ethylenebisformamide plasticized sample at RH 100%. EPTPSs proved to be having good thermal stability by thermogravimetric analysis (TGA). T_g (detected by differential scanning calorimetry (DSC)) of EPTPS was higher than that GPTPS.

Keywords: Thermoplastic starch; Ethylenebisformamide; Novel plasticizer

1. Introduction

It was widely accepted that the use of long-lasting polymers for short-lived applications (packaging, catering, surgery, hygiene), was not entirely adequate. This was not justified when increased concern exists about the preservation of ecological systems. Most of today's synthetic polymers were produced from petrochemicals and were not biodegradable. These persistent polymers were a significant source of environmental pollution, harming wildlife when they are dispersed in nature. Reaching the conditions of conventional plastic replacements by degradable polymers was of major interest for all the researchers. Starch, a biodegradable polymer, was one of the most promising materials to achieve this objective (Roberta & Cristina, 2002).

Thermoplasticized starch (TPS) was a biodegradable material based on starch, an inexpensive and natural renewable polysaccharide, which had been widely investigated as the substitute of petroleum-derived plastics. Native starch commonly existed in granule structure with about 15–45% crystallinity. Plastification process was the disruption of granular starch, which meant the transformation of the semi-crystalline granule into a homogeneous, rather amorphous material with the destruction of hydrogen bonds between the starch molecules, and synchronously with the formation of the hydrogen bonds between plasticizer and starch molecules. Disruption could be accomplished at the presence of appropriate plasticizer by applying thermomechanical energy in a continuous process. The combination of thermal and mechanical inputs could be obtained by extrusion, a common plastic processing technique. Under temperature and shearing, starch was plasticized. After the processing, a homogeneous molten phase was obtained.

Traditional plasticizers were polyols such as glycerol, glycol, xylitol, sorbitol, and sugars (Barret, Kaletunc, Rosenburg, & Breslauer, 1995; Fishman, Coffin, Konstance, Onwulata, 2000; Forssell, Mikkilä, Moates, Parker, 1998; Liu, Yi, & Feng, 2001; Wang, Shogren, & Carriere, 2000; Yu, Gao, & Lin, 1996). Some small molecules contain –CO–NH– functional group like urea (Kazuo, Isao, Toshiaki, Shin, Seichi and Yuuko, 1998) was also proved to be as plasticizer for the native starch. It was, however, a solid with little internal

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flexibility and hence urea-plasticized TPS became rigid and brittle. Recently, Ma (Ma & Yu, 2004a,b,c) reported that formamide or formamide/urea mixture could also plasticize native starch. Formamide could make thermoplastic starch more flexible, but the tensile failure stress was weak. They also found that the water resistant of formamide plasticized TPS was a little better than traditional glycerol plasticized one. In this paper, we utilize a novel plasticizer (ethylenebisformamide) (Sidney, Clifford, & Harry, 1962) to produce thermoplasticized starch and wished to obtain good mechanical properties and water resistance TPS. As a result, ethylenebisformamide was proved to be as a good plasticizer for the potato starch.

2. Experimental section

2.1. Materials

Potato starch (12% moisture) was obtained from Feima foodstuff Ltd (inner-Mongolia, China). The plasticizers, glycerol was purchased from Tianjin Chemical Reagent Factory (Tianjin, China) and ethylenebisformamide was synthesized in our lab.

2.2. Ethylenebisformamide synthesis

As a general procedure, ethylenediamine was added slowly to an excess of methyl formate cooled in ice. The solution was refluxed for 10 h and after standing overnight the products were isolated by filtration. The solids obtained by filtration were recrystallized from anhydrous ethyl alcohol, m.p. 108–110 °C was consistent to the lit (Sidney et al., 1962).

2.3. Preparation of GPTPS and EPTPS

The plasticizer was blended (3000 rpm, 2 min) with potato starch in the High Speed Mixer GH-100Y (made in China), until a homogeneous dispersion was obtained. Then, the mixture was placed overnight for the diffusion of the plasticizer into the granule. The ratio of plasticizers and potato starch (wt/wt) was 25:100 to 35:100. GPTPS and ethylenebisfomamide-plasticized TPS (EPTPS) were prepared as following: the mixtures were manually fed into the single screw Plastic Extruder SJ-25(s) (Screw Ratio L/D = 25:1, made in China) with a screw speed of 10 rpm. The temperature profile along the extruder barrel was 135, 140, 135, 135 °C (from feed zone to die). The die was a round sheet with the diameter 3 mm holes. The blends after preparation were stored in the sealed polyethylene bags.

2.4. Fourier transform infrared (FT-IR) spectroscopy

The IR spectra were measured with BIO-RAD FTS3000 IR Spectrum Scanner. The extruded TPS strips were pressured to the transparent slices in the Flat Sulfuration Machine, and tested by the reflection method.

2.5. Scanning electron microscopy (SEM)

The native wheat flour and the fracture surfaces of extruded TPS strips were performed with Scanning Electron Microscope Philips XL-3 (FEI Company, Hillsboro, Oregon, USA), operating at an acceleration voltage of 20 kV.

Native starch powders were suspended in acetone. The suspension drops were drawn on the glass flake, dried for removing the acetone, and then vacuum coated with gold for SEM. The GPTPS and EPTPS strip samples were cooled in liquid nitrogen, and broken immediately. The fracture faces were vacuum coated with gold for SEM.

2.6. Mechanical testing

Samples of 8 cm × 3 mm in size were cut from the extruded strips, pressured with the Flat Sulfuration Machine. The Testometric AX M350-10KN Materials Testing Machine was operated and a crosshead speed of 10 mm/min was used for tensile testing (ISO 1184-1983 standard). The data was averages of 5–8 specimens.

2.7. X-ray diffractometry

The extruded TPS strips were pressured at 10 MPa with the Flat Sulfuration Machine. After a period of storage time at several RHs, the slices were placed in a sample holder for X-ray diffractometry. The powders were packed tightly in the sample holder. X-ray diffraction patterns were recorded in the reflection mode in angular range 10–30° (2θ) at the ambient temperature by a BDX3300 diffractometer, operated at the Cu Kα wavelength of 1.542 Å. The radiation from the anode, operating at 36 kV and 20 mA, monochromized with a 15 μm nickel foil. The diffractometer was equipped with 1° divergence slit, a 16 mm beam bask, a 0.2 mm receiving slit and a 1° scatter slit. Radiation was detected with a proportional detector.

2.8. Water absorption

The samples were stored at different relative humidities (RH) for a period of time till equilibrium. The materials are dried silica gel, $MgCl_2$ saturated solution, substantive 35.64% $CaCl_2$ solution, NaCl saturated solution and distilled water, providing RH 0, 25, 50, 75, and 100%, respectively.

The original water contents (dry basis) of TPS were determined gravimetrically by drying small pieces of TPS at 105 °C overnight. At this condition, evaporation of the plasticizers was negligible. When TPS was stored for a period of time, its water content was calculated on the base of its original weight, its current weight and its original water content.

2.9. Thermogravimetric analysis (TGA)

TPS was cut into small pieces, which were tested by ZRY-ZP thermogravimetric analysis instrument (Beijing Plastic

Machinery Factory, Beijing, China). The TG analysis was carried out in the air. The samples were about 5–10 mg, the scope of testing temperature was from the room temperature to 510 °C and the heating rate was 15 °C/min.

2.10. Differential scanning calorimetry (DSC)

DSC measurements were carried out in a Perkin-Elmer DSC-7 (Perkin-Elmer Cetus, Norwalk, CT). Calibration was based on pure indium. An empty pan was used as reference. Prior to analysis, samples were placed at room temperature (RH 33%) for 1 month. Samples were scanned at a rate of 10 °C/min. Glass transition temperatures were determined from resulting thermograms at the onset temperature of step changes in heat flow observed during heating and identified as second-order transitions.

3. Results and discussion

3.1. FT-IR analysis

The analysis of FT-IR spectra of the blends enabled the hydrogen bond interaction to be identified (Aoi, Takasu, & Okada, 1998). On the basis of the harmonic oscillator model the reduction in force constant ((Δf could be represented by Eq. (1).

$$\Delta f = f_{\mathrm{p}} - f_{\mathrm{np}} = \frac{\mu\left(v_{\mathrm{p}}^2 - v_{\mathrm{np}}^2\right)}{4\pi^2} \tag{1}$$

where $\mu = m_1 m_2/(m_1 + m_2)$ corresponded to the reduced mass of the oscillator, v was the oscillating frequency and f was the force constant. The subscripts np and p denoted non-plasticized and plasticized oscillators, respectively. The reduction of force constant brought about by some interaction was directly related to the frequency (or wave number) shift of stretching vibrations. Thus, the lower the peak frequency the stronger was the interaction (Pawlak & Mucha, 2003).

The characteristic peak 1081 and 1157 cm^{-1} (Fig. 1(a)) was ascribed to C–O bond stretching of C–O–H group, where the peak was shifted to 1078 cm^{-1} and from 1148 to 1150 cm^{-1} (Fig. 1 (b–d)), which illustrated that OH group of starch took part in the hydrogen bond formation. Another peak at 1021 cm^{-1} attributed to C–O bond stretching of C–O–C group in the anhydroglucose ring (Fang, Fowler, Tomkinson, & Hill, 2002) shifted from 1016 to 1017. From the analysis of the peak style, the characteristic peak in 1081 and 1157 cm^{-1} had little change, and a double-peak appeared instead of the single peak of native starch at the peak 1021 cm^{-1}, which indicated that in the course of the hydrogen bond formation between plasticizer and starch, the H atom of the C–O–H group and the O atom of the C–O–C group in starch mainly participated in.

From the analysis above, ethylenebisformamide could form more stable hydrogen bond with starch than the strong action between hydroxy groups of starch molecules, thus starch was plasticized.

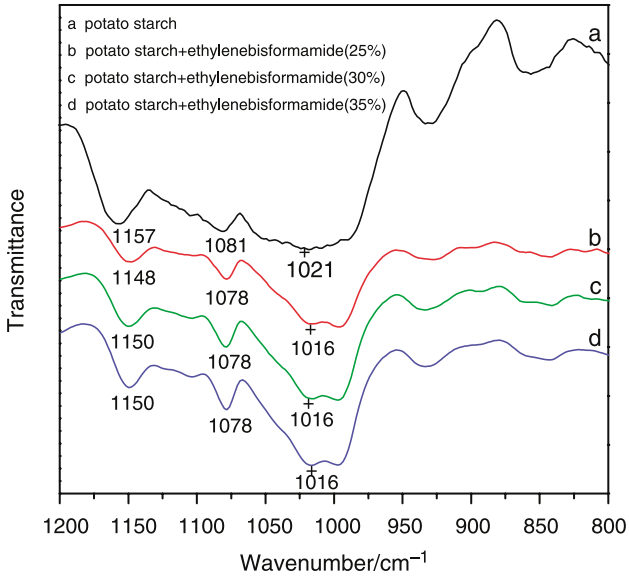

Fig. 1. FT-IR spectra of ethylenebisformaide plasticized TPS.

3.2. Scanning electron microscopy (SEM)

Stable hydrogen bond formed between ethylenebisformamide and starch by the analysis of FT-IR spectra because of the two –CO–NH– in the plasticizer and which could also weaken the hydrogen bond of the intermolecular and intramolecular in native starch consequently. A continuous phase was predicated to be formed under shear and pressure as a result. Compared with native potato starch granules (Fig. 2), the microcosmic morphology of the extruded TPS was shown in Fig. 3. TPS containing over 25% weight content of ethylenebisformamide could obtain a continuous phase, while a quantity of solid did not fuse into one continuous phase for TPS containing 25% weight content of plasticizer, but for TPS containing 30% plasticizer, the solid decreased drastically. It meant that enough plasticizer was necessary to form the homogeneous TPS. Due to the high shear and temperature conditions with the action of plasticizer, native potato starch granules were molten or physically broken up into small fragments.

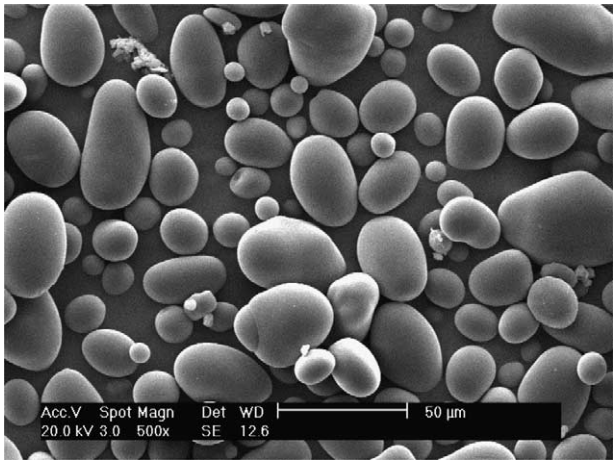

Fig. 2. SEM micrograph of native potato starch.

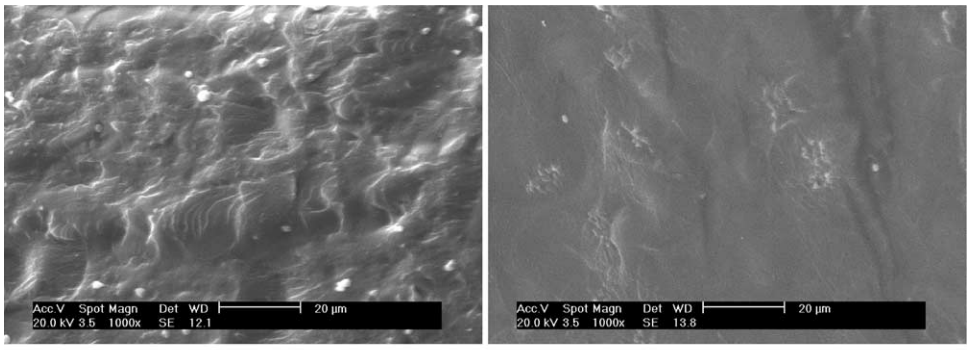

Fig. 3. SEM micrograph of ethylenebisformamide plasticized TPS.

Ethylenebisformamide was testified to disrupt intermolecular and intramolecular hydrogen bonds of the native potato starch and made it plastic.

3.3. Mechanical properties

The stress–strain curves of several TPS, which were plasticized with glycerol or different content of ethylenebisformamide, and then stored at RH 33% for 1 week after thermoplastic process, were shown in Fig. 4. The stress–strain diagrams of the materials showed the typical pattern of rubbery starch plastic materials reported previously (Van Soest & Knooren, 1997). The plots were essentially linear at low strain and curved towards the strain axis at higher strains, which endowed the EPTPS a flexible property. By the increase of the plasticizer content, ethylenebisformamide plasticized starch appeared to increase the elongation at break significantly with decrease of the stress. While the glycerol (30%) platicized potato starch (Fig. 4(a)) proved to be as a rigid and brittle material. It was obvious that the elongation at break of EPTPS was about seven times than that of GPTPS when the content of plasticizer was the same (30%), though the stress showed a decrease. This might be that there was a flexible chain –CH2–CH2– in the plasticizer so that the elongation at break increased with the increase of the plasticizer content, and it reached to 140% with the plasticizer content 35%.

3.4. Crystallization behavior

The X-ray diffraction patterns of native potato starch and original TPS (newly prepared) materials were shown in Fig. 5. Compared with native potato starch, the crystal behavior of TPS plasticized by ethylenebisformamide changed much. In the processing, plasticizer molecules entered into starch particles, replaced starch intermolecular and intramolecular hydrogen bonds, and destructed the crystallinity of starch. According to the earlier literatures (Zobel, 1988), there was a typical B-type crystallinity peak (about 17°) in the native starch (Fig. 5(a)). After the thermal process of the mixture of potato starch and ethylenebisfomamide (25%), B-style crystallinity disappeared and V_H-type crystallinity (the crystallinity between plasticizer and starch) was formed due to the inductive of the thermal process. However, with the increase of plasticizer content, V_H-type crystallinity became unconspicuous shown in Fig. 5(d,e). The reason must be that good dispersion of the starch molecular and ethylenebisformamide when the content of the ethylenebisformamide increased made

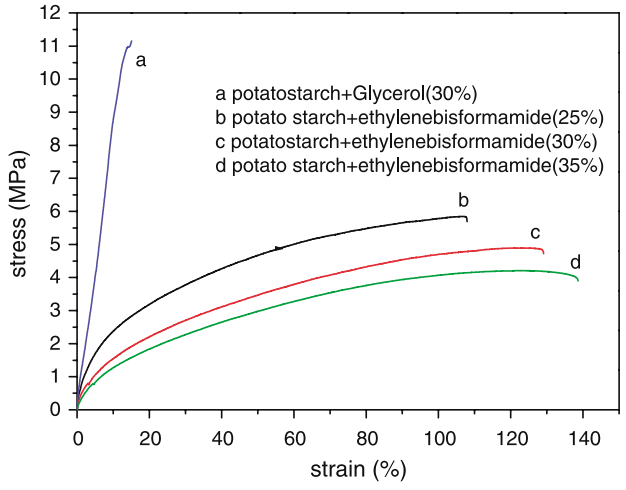

Fig. 4. The stress–strain curves of TPS with different plasticizer content.

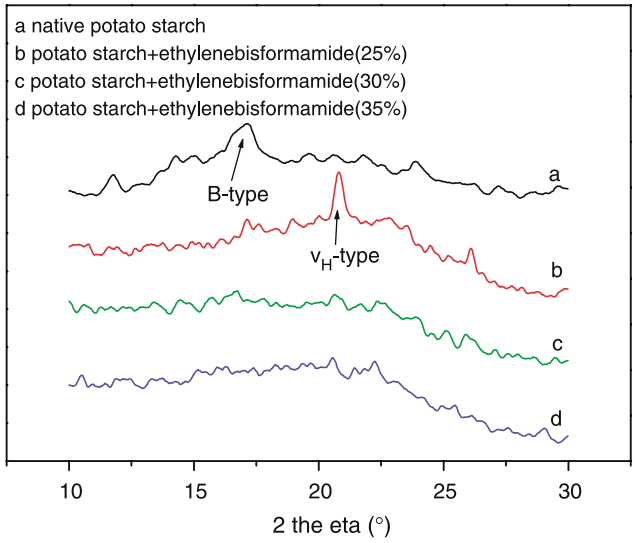

Fig. 5. The diffractograms of native potato starch, GPTPS and EPTPS.

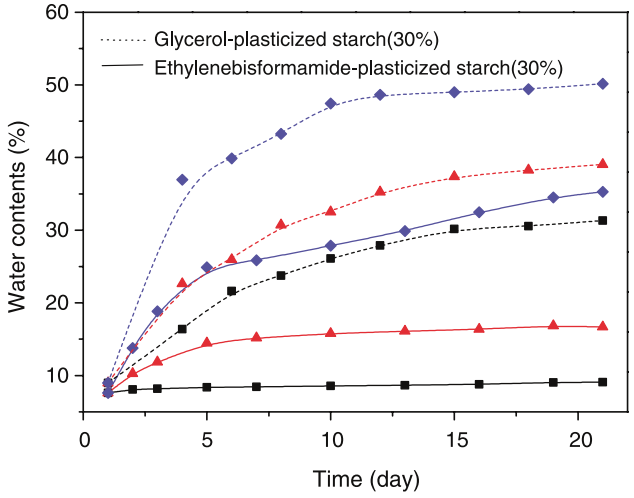

Fig. 6. Water contents of GPTPS and EPTPS with the storage times at different RHs. (RH 50, 75 and 100% from the bottom to the top).

the starch molecular more pliable, and there was little odd to form a V_H-type crystallinity under shear and pressure at the same thermal process.

3.5. Water absorption

Water absorption of GPTPS and EPTPS containing 30% plasticizer at different RHs from 50 to 100% were shown in Fig. 6. From the curve of Fig. 6 we found that the balance water contents of EPTPS were evident lower than GPTPS. After 21 days equilibrium, the utmost balance water contents of the GPTPS and EPTPS were 31.3, 39.1, 50.2% and 9.1, 16.7, 35.3% (corresponding to the RHs 50, 75, 100%), respectively. The drastically decrease of the water content of EPTPS compared with GPTPS indicated that EPTPS was a better water resistant material. The causation of this phenomenon must be that ethylenebisformamide formed stronger hydrogen-bond with potato starch which restrained the water molecule to combine to the plasticizer or to the potato starch. Fig. 7 was the

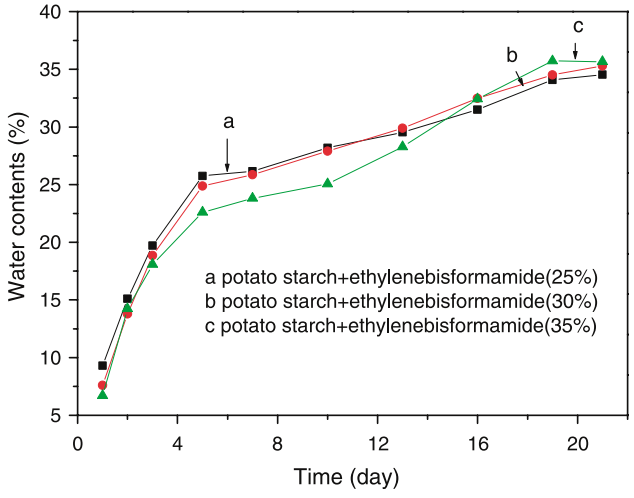

Fig. 7. Water contents of EPTPS with different platicizer contents for TPS at RH100%.

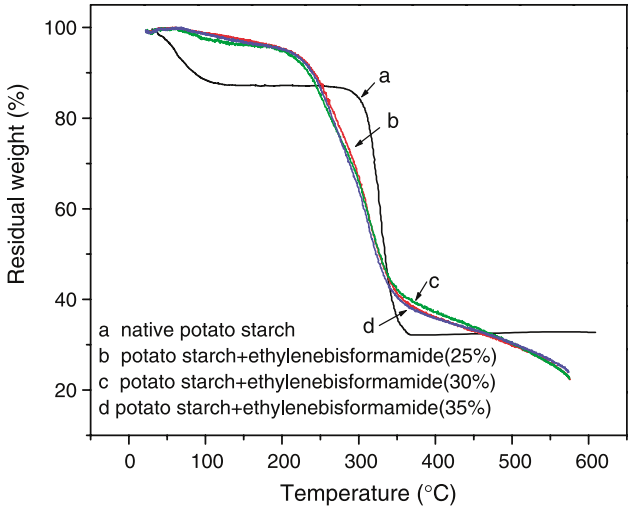

Fig. 8. TGA curves of EPTPS and native potato starch.

curve of EPTPS containing different plasticizer contents from 25 to 35% at RH 100%. The water absorption of EPTPF had little difference for these three TPSs as shown in Fig. 7. The result also proved to be that stronger hydrogen-bond formed between plasticizer and the potato starch when the content of ethylenebisformamide content was higher than 25%. It was harder for water molecular to penetrate into the EPTPS, as a result, plasticizer–water interactions and starch–water interactions were very weak relatively, so that the EPTPS presented lower water absorption.

3.6. Thermal stability

Fig. 8 was the TGA experimental result. The forms of the mass loss curves were similar for the EPTPSs containing plasticizer weight from 25 to 35%. Since the boiling points of the plasticizers are above 100 °C, mass loss below 100 °C was mainly ascribed to water loss and from 100 °C to the decomposition onset temperature was related to the volatilization of both water and plasticizers. As shown in Fig. 8, the mass loss of EPTPSs with plasticizer from 25 to 35% were similar to each other, which indicated that the content of the plasticizer content have little effect on the thermal stability. Compared with native potato starch, EPTPS could restrain the water loss below 100 °C because of the interaction between water and EPTPS.

3.7. Differential scanning calorimetry (DSC)

The DSC measurements served to determine the relaxational transition of the TPS. As shown in Fig. 9, the upper transition of both for EPTPS and GPTPS could be linked to the TPSs glass transition. The lower one could be connected to plasticizers glass transition and was independent of the content of the plasticizer (Lourdin, Bizot, Colonna, 1997), which was mainly determined by the variety of the plasticizer. The T_g of GPTPS and EPTPS shifted from 25 to 49 °C. This evolution could be ascribed to the strong interactions between the starch

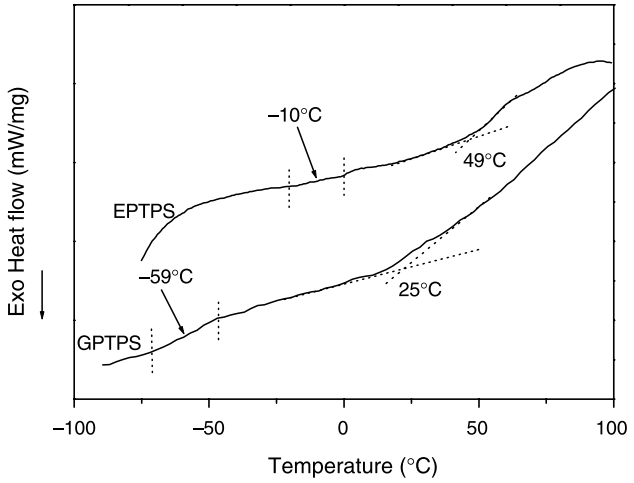

Fig. 9. DSC scans for EPTPS and GPTPS.

and plasticizer. For EPTPS, more strong hydrogen bonds formed between ethylenebisformamide and starch, which decreased starch chain mobility and consequently increase the matrix glass transition. The lower relaxational transition of EPTPS (−10 °C) was higher than that GPTPS (−59 °C), the reason must be that melt point of ethylenebisformamide was 108–110 °C, whereas it was a liquid for glycerol at room temperature.

4. Conclusion

Etylenebisformaide, synthesized in our lab was proved to be as a novel and good plasticizer for the potato starch. It formed stable hydrogen bond with starch by the analysis of the FT-IR spectra. From the analysis of SEM, native potato starch granules were proved to transfer to a continuous phase with the destruction of all crystallinity. Tensile testing experimental indicated that the elongation increased significantly with a little decrease of the tensile strength compare with the GPTPS. It was noticeable that EPTPS was a better water resistant material. Good thermal stability had also been testified by thermogravimetric analysis. T_g of EPTPS testified by Differential scanning calorimetry (DSC) was higher than that GPTPS, this phenomenon could be explained by that more strong hydrogen bonds formed between ethylenebisformamide and starch.

All in all, we had developed a novel plasticizer for the limited plasticizer families (usually polyols), further investigation should be carried out for the research of EPTPS, which would be practical to extend TPS application scopes.

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