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Urea and ethanolamine as a mixed plasticizer for thermoplastic starch

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Abstract

Mixtures of urea and ethanolamine were used as plasticizers for preparing thermoplastic starch (TPS) in a single-screw extruder. The interaction between urea/ethanolamine and starch was investigated using Fourier Transform Infrared (FT-IR). Glass transition temperature of TPS was tested by Differential scanning calorimetry (DSC). Both FT-IR and DSC proved that the mixture of urea and ethanolamine could form more stable and strong hydrogen bonds with starch molecules than the conventional plasticizer, glycerol. By Scanning Electron Microscope (SEM) native starch granules were proved to transfer to a continuous phase. The thermal stability, mechanical properties and starch retrogradation behavior were also studied by TG (Thermal Gross), tensile testing and X-ray Diffraction (XRD), respectively. TPS plasticized by urea (15 wt/wt%) and ethanolamine (15 wt/wt%) showed a better thermal stability and mechanical properties than conventional TPS plasticized by glycerol. Moreover, the tensile stress, strain and Energy Break, respectively, reached 9.00 MPa, 34.4% and 1.34 N m. At the same time, this mixed plasticizer could effectively restrain the retrogradation of starch and urea.

Keywords: Thermoplastic starch; Retrogradation; Ethanolamine; Urea

1. Introduction

Much effort (Averous, Fauconnier, Moro, & Fringant, 2000; Fang & Hanna, 2001; Martin & Averous, 2001) had recently been made to develop biodegradable materials because of the worldwide environment and resources problems resulted from petroleum-derived plastics. Starch, a natural renewable polysaccharide obtained from a great variety of crops, was one of the promising raw materials for the production of biodegradable plastics (Petersen, Væggemose, & Bertelsen, 1999). However, native starch commonly existed in granule structure with about 15–45% crystallinity (Zobel, 1998), and starch-based materials were susceptible to aging and starch re-crystallization (retrogradation). TPS plasticized with glycerol, a conventional TPS, was thought to tend to retrogradation after being stored for a period of time, and this retrogradation embrittled TPS (Van Soest & Knooren, 1997). Urea was proven to prevent starch retrogradation. It was, however, a solid with little internal flexibility and hence urea-plasticized TPS became rigid and brittle (Stein & Greene, 1997).

It was hypothesized that the introduction of another plasticizer for starch, which was a good solvent for urea, prevented urea from separating out. Preliminary studies in our laboratory had shown that Ethanolamine could availably suppress the retrogradation of thermoplastic starch and make thermoplastic starch more flexible, but the tensile failure stress was weaker than the conventional glycerol-plasticized TPS (GPTPS). In this paper, a combination of urea and ethanolamine would effectively restrain TPS retrogradation, improve mechanical properties of TPS and prevent urea from separating out. It was suspected, therefore, that this mixture might be a better plasticizer for starch.

In this paper, GPTPS was regarded as the reference. The hydrogen bonding interaction between urea/ethanolamine and starch using FT-IR was described. And the properties of TPS plasticized by urea and ethanolamine, such as thermal stability, starch retrogradation behavior and mechanical properties, were also studied.

2. Experimental section

2.1. Materials

Cornstarch (10% moisture) was obtained from Langfang Starch Company (Langfang, Heibei, China). The plasticizers (Chemical Purity), glycerol, ethanolamine and urea, were

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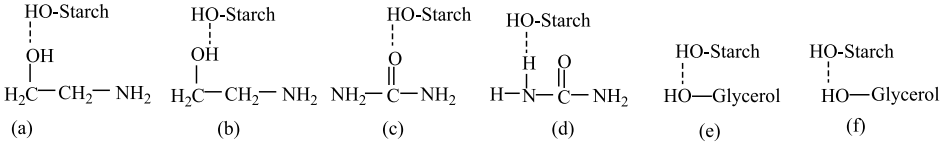

Fig. 1. The styles of the most possible hydrogen bonds in EPTPS, UPTPS and GPTPS.

purchased from Tianjin Chemical Reagent Factory (Tianjin, China).

2.2. Plasticization

The plasticizers were blended (3000 rpm, 2 min) with cornstarch in the High Speed Mixer GH-100Y (made in China), and then stored overnight. The ratio of plasticizers and cornstarch (wt/wt) was 30:100. When two plasticizers were used together, another step for the pre-mixture of them was required. GPTPS, urea-plasticized TPS (UPTPS), ethanolamine-plasticized TPS (EPTPS) and urea/ethanolamine-plasticized TPS (UEPTPS) 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 20 rpm. The temperature profile along the extruder barrel was 120, 130, 130, 110 °C (from feed zone to die). The die was a round sheet with the diameter 3 mm holes.

The contents of materials in this paper were all referred to weight contents.

2.3. 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 with the thickness of around 0.2 mm in the Flat Sulfuration Machine, and tested by the transmission method.

2.4. Scanning electron microscope (SEM)

The native starch and the fracture surfaces of extruded TPS strips were performed with Scanning Electron Microscope Philips XL-3, 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. TPS strip samples were cooled in liquid nitrogen, and then broken. The fracture faces were vacuum coated with gold for SEM.

2.5. Thermal analysis (TG)

TPS was cut into small pieces, which were tested by ZRY-ZP thermal analysis instrument (Beijing Plastic Machinery Factory, Beijing, China). The samples were about 5–10 mg in a sealed aluminum pan, the scope of testing temperature was from the room temperature to 500 °C and the heated rate was 15 °C/min.

2.6. 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 week. Samples were scanned at a rate of

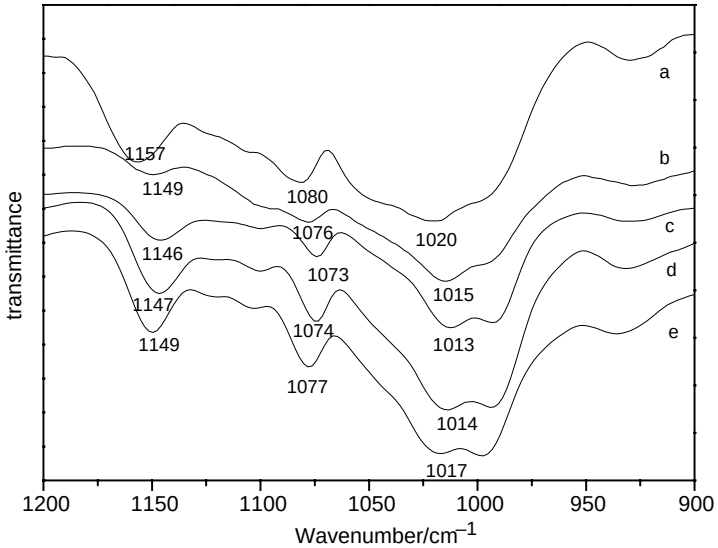

Fig. 2. The FT-IR spectra of TPS with different plasticizers: (a) native starch; (b) TPS containing 30% glycerol; (c) TPS containing 30% urea; (d) TPS containing 10% urea and 15% ethanolamine; (e) TPS containing 30% ethanolamine.

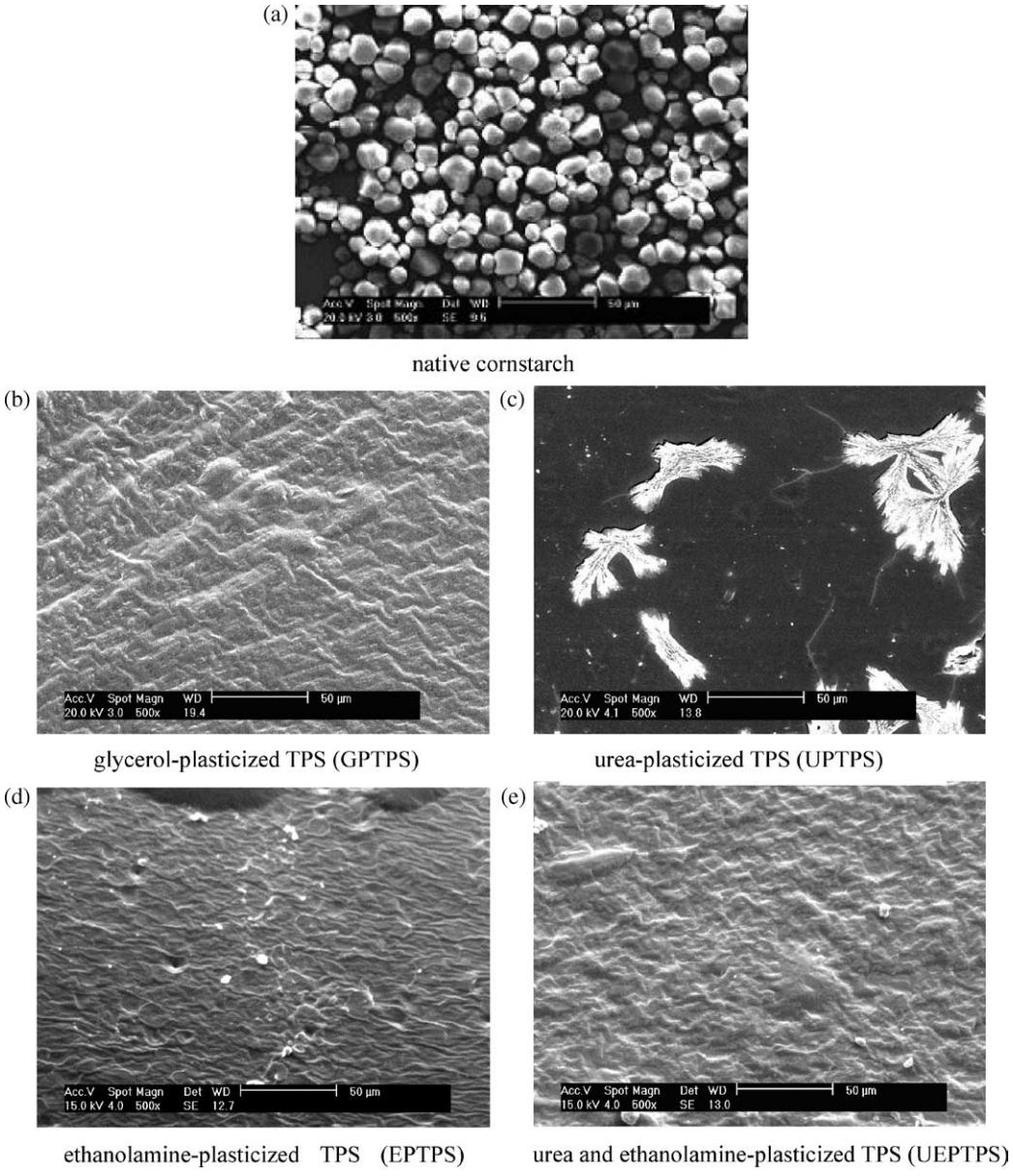

Fig. 3. SEM micrograph of native starch granules and the fracture face of TPS.

10 °C/min in sealed pan. Glass transition temperatures were determined from resulting thermograms as the midpoint between onset and end temperatures of step changes in heat flow observed during heating and identified as second-order transitions.

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. 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.

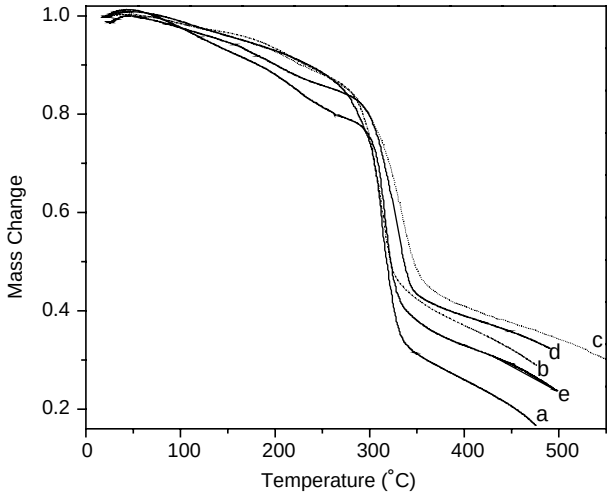

Fig. 4. The TG curves of several TPS. (a) TPS containing 30% glycerol; (b) TPS containing 30% urea; (c) TPS containing 15% urea and 15% ethanolamine; (d) TPS containing 10% urea and 20% ethanolamine; (e) TPS containing 30% ethanolamine.

3. Results and discussion

3.1. The hydrogen bonding interaction

Native starch contained two different molecular structures: the linear (1,4)-linked α-D-glucan amylose and highly (1,6)-branched α-D-glucan amylopectin (Garci'a-Alonso, Jime'ne-z-Escrig, Mart'in-Carron, Bravo, & Saura-Calixto, 1999). There was a lot of hydrogen interaction in native starch, which restrained the movement of starch molecules and made it difficult to process starch without plasticizers. Under the action of high temperature, shear and plasticizers, starch could be processed into a mouldable thermoplastic, a material known as thermoplastic starch (TPS) (Forssell, Mikkilä, Moates, & Parker, 1997). During the thermoplastic process, added plasticizers and water contained in native starch played an indispensable role (Hulleman, Janssen, & Feil, 1998), because the plasticizers could form the hydrogen bonds with starch, take the place of the strong action between hydroxyl groups of starch molecules, and make starch thermoplastic. OH groups in ethanolamine, O=C and NH_2 groups in urea and OH groups in glycerol could form hydrogen bonds with starch. The styles of the most possible hydrogen bonds in EPTPS, UPTPS and GPTPS were shown in Fig. 1.

Formation of homogeneous TPS was a result of strong interactions by hydrogen bonds between starch and plasticizers. The analysis of FTIR spectra of the blends enabled hydrogen bond interactions to be identified (Ma & Yu, 2004). Moreover, the lower the peak frequency of C–O group in starch was, the stronger the interaction between starch and plasticizers was.

FT-IR spectra for TPS with different plasticizers were shown in Fig. 2. There were three characteristic peaks of starch between 990 and 1160 cm^{-1}, attributed to C–O bond stretching. The peaks at around 1150 and 1080 cm^{-1} were characteristic of C–O–H in starch, while the peak between 990 and 1030 cm^{-1} was characteristic of the anhydroglucose ring O–C stretch (Fang, Fowler, Tomkinson, & Hill, 2002). As shown in Fig. 2, compared to three characteristic peaks of native starch, those of TPS located at the lower wave number, and the double-peak appeared at between 990 and 1030 cm^{-1} in c, d and e instead of the single peak of native starch (a in Fig. 2), because glycerol, ethanolamine, urea and the mixture (urea and ethanolamine) could 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, newly formed between urea/ethanolamine and C–O group of starch. The more stable and strong the hydrogen bonds were, the more the correlative peaks shifted and the peak styles changed (Pawlak, & Mucha, 2003). Therefore, as revealed by FT-IR, the mixture of 15% urea and 15% ethanolamine could form stronger interaction with starch than glycerol or ethanolamine.

3.2. Scanning electron microscopy (SEM)

The mixture of urea and ethanolamine could form stable hydrogen bond with starch by the analysis of FTIR spectra because ethanolamine and urea weakened the hydrogen bond of the intermolecular and intramolecular in native starch. Due to the high shear and temperature conditions with the action of plasticizer, native starch granules were molten or physically broken up into small fragments. A continuous phase was predicated to be formed under shear and pressure as a result. Compared with native starch granules (in Fig. 3a), the microcosmic morphology of the extruded TPS was shown in Fig. 3b–e. As shown in Fig. 3c, urea crystal separated out in UPTPS, while urea crystal of UEPTPS (urea/ethanolamine wt 15/15%) was invisible in Fig. 3e. As a good solvent for urea, ethanolamine and water in starch could dissolve urea and prevent crystallization of urea, which generally made TPS materials rigid and brittle.

Table 1
The effect of the proportion of urea/ethanolamine on the onset of decomposition and mass loss at onset temperature in several in the TG experiments of TPS

Plasticizers (wt/wt) Urea/ethanolamine	30%/0%	15%/15%	10%/20%	0%/30%	Glycerol 30%
Onset temperature (°C)	292.8	300.8	301.2	295.9	292.5
Mass loss (%)	16.2	17.2	17.9	23.3	18.8
Midpoint temperature (°C)	310.1	328.4	320.8	316.4	314.2

3.3. Thermal stability

Fig. 4 presented the TG experimental results. The behavior of the mass loss curves was similar in several TPS. Because the boiling points of the plasticizer outclassed 100 °C, the mass loss below 100 °C was mainly ascribed to water loss. And the mass loss from 100 °C to the onset temperature was related to the volatilization of both water and plasticizers. So the difference in the decomposition onset and mass loss at onset temperature was mainly due to the different volatility of several plasticizers in TPS. As shown in Fig. 4a,b and e, ethanolamine molecule was more volatile than glycerol and urea. However, the mixtures of urea and ethanolamine were able to improve the onset of decomposition and reduce mass loss at onset temperature (compared with Fig. 4c–e). The volatility of both ethanolamine and urea was reduced, because ethanolamine was a good solvent for urea, and the mixtures of urea and ethanolamine could form the strong interaction with starch.

In the view of onset temperature and midpoint decomposition temperature (as shown in Table 1), the proper proportional mixture of urea and ethanolamine (for instance, 20 wt/wt% urea/10 wt/wt% ethanolamine and 15 wt/wt% urea/15 wt/wt% ethanolamine) could obviously ameliorate TPS thermal stability.

3.4. Differential scanning calorimetry (DSC)

The DSC measurements served to determine the relaxational transition of the TPS. The glass transition temperature, T_g was shown in Fig. 5, DSC curves of TPS. T_g of GPTPS, EPTPS and UPTPS were, respectively, 28, 25 and 45 °C, while T_g of UEPTPS containing 15% urea and 15% ethanolamine was 37 °C, located between EPTPS and UPTPS. This evolution could be ascribed to the strong interactions between the starch and plasticizer. In TPS the strong hydrogen bonds formed between plasticizers and starch, which decreased starch chain mobility and consequently increased the matrix glass transition. In the views of T_g, as the plasticizer, this mixture of 15% urea and 15% ethanolamine could form stronger interaction with starch than glycerol or ethanolamine. This result was similar to FT-IR result.

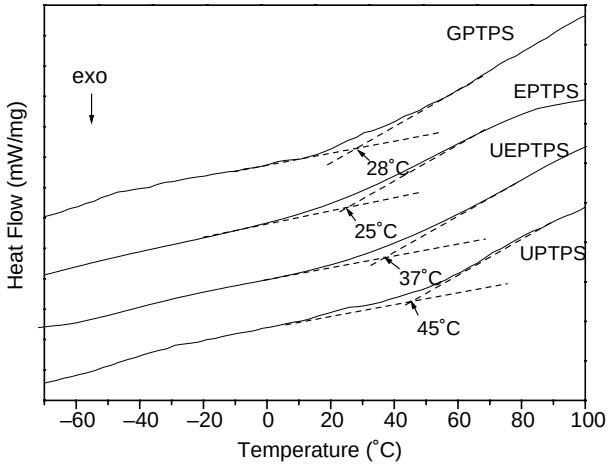

Fig. 5. DSC curves of TPS.

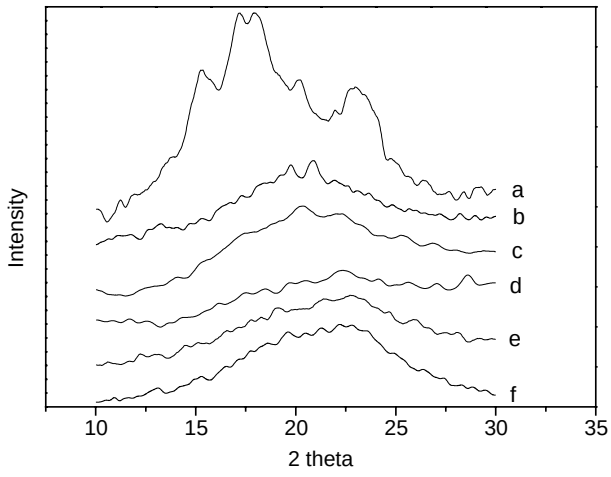

Fig. 6. TPS after thermoplastic process. (a) native starch; (b) GPTPS; (c) EPTPS; (d) UEPTPS (urea/ethanolamine, 15/15); (e) UEPTPS (urea/ethanolamine, 25/5); (f) UPTPS.

3.5. Retrogradation

The X-ray diffraction patterns of TPS, plasticized by glycerol, ethanolamine and urea, were shown in Fig. 6. There were no crystals of native starch in newly prepared TPS. In thermoplastic process ethanolamine and/or urea molecules entered into starch granules, then should replace starch intermolecular and intramolecular hydrogen bonds and destruct the crystal of native starch. So their effect was the same as glycerol. When these TPS were stored at RH50% for 25 days, TPS showed no obvious crystal peaks except GPTPS in Fig. 6. As it was well known, GPTPS, prone to retrogradation, showed a V_H style crystal peak (Van Soest & Vliegenthart, 1997) (e in Fig. 7). According

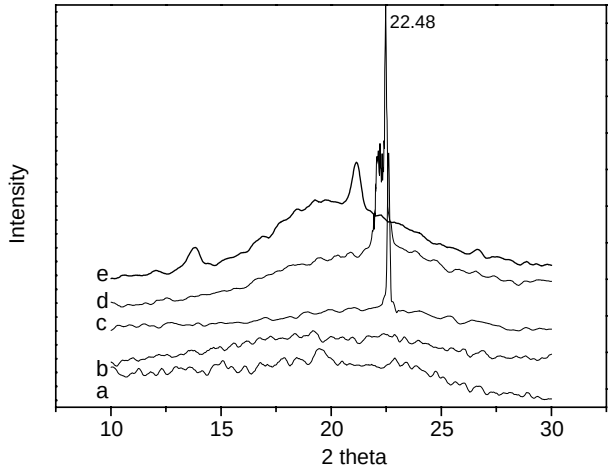

Fig. 7. The diffractograms of TPS stored at RH50% for 25 days. (a) EPTPS; (b) TPS containing 15% urea and 15% ethanolamine; (c) TPS containing 25% urea and 5% ethanolamine; (d) UPTPS; (e) GPTPS.

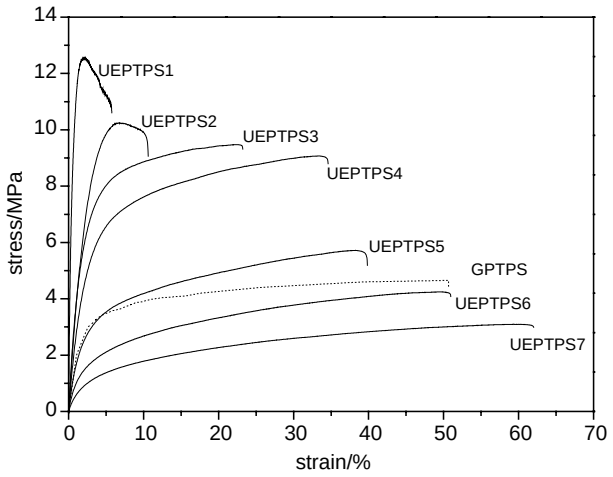

Fig. 8. The stress–strain curves of several TPS plasticized with different plasticizers UEPTPS1-7 denoted UEPTPS with the following proportion of urea and ethanolamine.

to J.J.G van Soest (Van Soest, Hulleman, de Wit, & Vliegenthart, 1996), V_H type was a single-helical structure 'Inclusion Complex', made up of amylose and glycerol. Urea and ethanolamine could restrain starch retrogradation, because they could form more strong and stable hydrogen bonds with starch than glycerol according to FT-IR and DSC analysis, and then prevent starch molecules from interacting and crystallizing again. The mixed plasticizers of urea and ethanolamine could also effectively suppress the retrogradation of TPS (b and c in Fig. 7), as urea did. The crystal peaks (c and d in Fig. 7) at around 22.5° were ascribed to urea crystallinity. When the ratio of ethanolamine to urea reached above 1, UEPTPS would become a stable system without the separating of urea.

3.6. Mechanical testing

The stress–strain curves of TPS, which were plasticized with only urea, ethanolamine, glycerol or the mixture of urea and ethanolamine with different proportions, and then stored at RH = 33% for 1 week after thermoplastic process, were shown in Fig. 8. The stress–strain diagrams of the materials showed the typical pattern of rubbery starch plastic materials reported previously (Van Soest & Knooren, 1997) except UEPTPS1. The plots were essentially linear at low strain and curved towards the strain axis at higher strains. TPS plasticized by only urea was a brittle glassy material but rigid. Urea could destroy the interaction of starch molecules more effectively than ethanolamine and glycerol during thermoplastic process, and then starch molecules were so flexible that starch molecules were packed too tightly without enough space for the segmental motion at room temperature. It was necessary for starch segmental motion to employ additional force, even up to the break strength of TPS, so UPTPS was brittle but rigid. A quantity of ethanolamine, substituting part of urea, could dilute this effect and improve the toughness (UEPTPS 3, UEPTPS 4 and UEPTPS 5 in Fig. 8). Ethanolamine could make cooled TPS retain enough free volume for the segmental motion, so EPTPS was tough but weak (UEPTPS 7 in Fig. 8). The mixture of ethanolamine and urea in the appropriate proportion (UEPTPS 4 in Fig. 8) appeared to increase the elongation at break.

The effects of the mixed proportion of urea and ethanolamine (maintaining a constant total contents of 30%) on UEPTPS mechanical properties were shown in Fig. 8 and Table 2. For TPS plasticized by urea alone, stress peak was 12.55 MPa and Youngs modulus was up to 1664 MPa, but strain peak and Energy Break were only 5.7% and 0.32 N m respectively. A small quantity of ethanolamine (10%) could improve the strain and Energy Break of TPS well, but stress and modulus dropped much. For EPTPS, stress, Youngs modulus and Energy Break were low although strain could reach 61.6%. Fig. 8 indicated that the superfluous ethanolamine intenerated TPS while the redundant urea rigidified and embrittled TPS. The most appropriate weight proportion was 15% urea and15% ethanolamine. This TPS showed good mechanical properties with the highest values of Energy Break as well as the favored stress, strain and Youngs modulus. The mechanical parameters of TPS plasticized by 15% urea and 15% ethanolamine were compared with those of TPS plasticized by glycerol (30 wt/wt%) as listed in Table 3. The former was superior to TPS plasticized by glycerol (30 wt/wt%) in mechanical properties except strain peak when they were stored at RH = 33% for 1 week.

Table 2
The effect of the proportion of urea and ethanolamine contents on the mechanical properties of UEPTPS

	Starch/ethanolamine/urea	Stress (MPa)	Strain (%)	Youngs moduls (MPa)	Break energy (N m)
UEPTPS 1	100/0/30	12.55	5.7	1664	0.32
UEPTPS 2	100/5/25	10.20	10.4	337	0.44
UEPTPS 3	100/10/20	9.44	13.0	315	0.97
UEPTPS 4	100/15/15	9.00	34.4	236	1.34
UEPTPS	100/20/10	5. 7	39.7	134	0.92
UEPTPS 6	100/5/25	4.2	50.6	102	0.85
UEPTPS 7	100/30/0	3.1	61.6	57	0.75

Table 3
The mechanical parameters of TPS plasticized by urea (15 wt/wt%) and ethanolamine (15 wt/wt%) (1) and by glycerol (30 wt/wt%) alone (2) stored at RH = 33% for 1 week

	Stress peak (MPa)	Strain peak (%)	Stress yield (MsPa)	Strain yield (%)	Energy break (N m)	Youngs modulus (MPa)
1	9.00	34.4	6.71	7.4	1.34	236
2	4.63	50.5	3.60	3.3	1.05	184

4. Conclusion

Mixtures of urea and ethanolamine used as a plasticizer could obviously ameliorate thermal stability, mechanical properties and retrogradation of TPS. These phenomena could be explained by the following two reasons. First, as proved by FT-IR and DSC analysis, the mixture of urea and ethanolamine could form more stable and strong hydrogen bonds with the hydroxyl group of starch molecules than the conventional plasticizer, glycerol. Second, ethanolamine was a good solvent for urea and then both of them could exist in molecular form in TPS. With effectively restraining starch retrogradation, TPS plasticized by urea (15 wt/wt%) and ethanolamine (15 wt/wt%) showed a better thermal stability and mechanical properties. Moreover, the tensile stress, strain and Energy Break could respectively reach 9.00 MPa, 34.4% and 1.34 N m.

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