Urea and formamide as a mixed plasticizer for thermoplastic starch

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Abstract: Mixtures of urea and formamide were tested as plasticizers for thermoplastic starch (TPS). The hydrogen bonding interactions between urea/formamide and starch were investigated by using Fourier-transform infrared spectroscopy (FT-IR). The thermal stability, mechanical properties and starch retrogradation behavior were also studied by thermogravimetric analysis (TGA), tensile testing and X-ray diffraction (XRD), respectively. TPS plasticized by urea (20 wt%) and formamide (10 wt%) showed better thermal stability and water resistance than conventional TPS plasticized by glycerol. Moreover, the tensile stress, strain and energy at break, respectively, reached 4.83 MPa, 104.6% and 2.17 N m after storing in an atmosphere of relative humidity (RH) of 33 % for one week. At the same time, this mixed plasticizer could effectively restrain the retrogradation of starch.

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Keywords: thermoplastic starch; retrogradation; formamide; urea

INTRODUCTION

Many efforts¹⁻³ have recently been made to develop biodegradable materials because of the worldwide environment and resources problems resulting from petroleum-derived plastics. Starch, a natural renewable polysaccharide obtained from a great variety of crops, is one of the most promising raw materials for the production of biodegradable plastics.⁴ Starch contains two different molecular structures, ie the linear (1,4)-linked α -D-glucan amylose and highly (1,6)branched α -D-glucan amylopectin.⁵ Native starch commonly exists in a granular structure with about 15-45 % crystallinity.⁶ Under the action of high temperature and shear, starch can be processed into a moldable thermoplastic, a material known as thermoplastic starch (TPS).⁷ During the thermoplastic process, water contained in starch and the added plasticizers play an indispensable role,8 because the plasticizers can form hydrogen bonds with the starch, replacing the strong interactions between the hydroxyl groups of the starch molecules, and thus making starch thermoplastic. However, starch-based materials are susceptible to ageing and starch recrystallization (retrogradation). TPS plasticized with glycerol, a conventional TPS, was thought to tend to retrograde after being stored for a period of time, and this retrogradation embrittled the TPS.9 Urea has been proven to prevent retrogradation. The latter is, however, a solid with little internal flexibility and hence urea-plasticized TPS becomes rigid and brittle.¹⁰

Preliminary studies in our laboratory have shown that formamide could suppress the retrogradation of thermoplastic starch and make it more flexible, although the tensile failure stress was lower than that of conventional glycerol-plasticized TPS (GPTPS). Since formamide is a good solvent for urea, it was hypothesized that a combination of urea and formamide would effectively reduce TPS retrogradation and improve its mechanical properties. It was suspected, therefore, that this mixture might be a better plasticizer system for starch.

In this present paper, GPTPS is regarded as the reference material. The hydrogen bonding interactions between urea/formamide and starch, studied by using Fourier-transform infrared (FT-IR) spectroscopy, are described. In addition, the properties of TPS plasticized by urea and formamide, such as thermal stability, mechanical properties, starch retrogradation behavior and water absorption, are also presented.

EXPERIMENTAL

Materials

Corn starch (11 % moisture) was obtained from the Langfang Starch Company (Langfang, Heibei, China). The plasticizers, ie glycerol, formamide and urea, were purchased from the Tianjin Chemical Reagent Factory (Tianjin, China).

Plasticization

The plasticizers were blended (3000 rpm, 2 min) with corn starch in a GH-100 high-speed mixer (Beijing Plastic Machinery Factory, Beijing, China), and then stored overnight. The ratio of plasticizers and corn

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starch (wt/wt) was 30:100. When two plasticizers were used together, another step for the pre-mixture preparation was required. GPTPS, urea-plasticized TPS (UPTPS), formamide-plasticized TPS (UPTPS) and urea/formamide-plasticized TPS (UFPTPS) were prepared as follows. The mixtures were manually fed into a single-screw SJ-25(s) plastic extruder (screw ratio, l/d = 25:1, Beijing Plastic Machinery Factory, Beijing, China) with a screw speed of 20 rpm. The temperature profile along the extruder barrel was 120 °C, 130 °C, 130 °C and 110 °C (from feed zone to die). The die was a round sheet with 3 mm diameter holes.

Fourier-transform infrared spectroscopy

IR spectra were recorded with a BIO-RAD FTS3000 IR spectrometer. The extruded TPS strips were pressed into transparent slices, with a thickness of around 0.2 mm, in a flat sulfuration machine (Flat Sulfuration Machine BL, Beijing Plastic Machinery Factory, Beijing, China), with measurements being made in the transmission mode.

Storage conditions and water content

In order to analyse the effect of environmental humidity on the tensile properties and TPS retrogradation, the samples for mechanical testing were stored in closed containers in the presence of different compounds, namely, dried silica gel, a saturated MgCl₂ solution, a 35.64 % CaCl₂ solution, a saturated MaCl solution and distilled water (providing relative humidities (RHs) of 0, 33, 50, 75 and 100 %, respectively) at 20 °C for 5 or 10 days. The samples for X-ray diffractometry were stored at 50 % RH and then tested every few days.

The original water contents (dry basis) of TPS were determined gravimetrically by drying small pieces at 105 °C overnight. Under these conditions, evaporation of the plasticizers was negligible.¹¹ When TPS was stored for a period of time, its water content was calculated on the basis of its original weight, its current weight and its original water content.

Mechanical testing

Samples, 8 cm in length and 3 mm in diameter were cut from the extruded strips, and pressed with the flat sulfuration machine. A testometric AX M350-10KN (The Testometric Company Ltd, Rochdale, UK), materials testing machine, operated at a crosshead speed of 10 mm min^{-2} , was used for tensile testing (ISO 1184-1983 Standard). The data reported were averages from 5–8 specimens.

X-ray diffractometry

The extruded TPS strips were pressed at 10 MPa with the flat sulfuration machine. After periods of storage time at different RHs, the samples 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 over the angular range $10-30^{\circ}(2\theta)$ at ambient temperature with a BDX3300 diffractometer, operated at the CuK α wavelength of 1.542 Å. The radiation from the anode, operated at 36 kV and 20 mA, was then passed through a monochromater made of a 15 µm nickel foil. The diffractometer was equipped with a 1° divergence slit, a 16 mm beam bar (raster), a 0.2 mm receiving slit and a 1° scatter slit. The radiation was detected with a proportional detector.

RESULTS AND DISCUSSION Hydrogen bond interactions

Compared with the hydroxyl group in glycerol, the amino group is advantageous to the formation of hydrogen bonds with starch, as it destroys the original hydrogen bonds between starch molecules and makes it thermoplastic. To estimate the difference in the hydrogen bond-forming ability among formamide, urea and glycerol, we took glycerol and formamide as examples. The forms of the most probable hydrogen bonds in both FPTPS and GPTPS are shown in Fig 1. When the hydrogen-bond acceptor is H in the OH group in starch, O, as the electron donor, in the carbonyl group of formamide (Fig 1a) has a higher electronegativity than O in the hydroxyl group of glycerol (Fig 1c), as the electron donating effect of the carbonyl double bonds increases the electron cloud density of O in the carbonyl group. When the hydrogen-bond donor is O in the OH group in starch, the H in the amino group of formamide (Fig 1b), ie the electron acceptor, has a lower electronegativity than H in the hydroxyl group of glycerol (Fig 1d). Thus, the order of the hydrogen-bond-forming ability is as follows: (a) > (c) and (b) > (d). Each urea molecule has two amino groups, and so it can form more stable hydrogen bonds with starch than formamide. Therefore, the resulting order of the hydrogen-bondforming ability with starch molecules is as follows: urea > formamide > glycerol.

In the IR spectrum of starch, there are three characteristic peaks between 990 and 1160 cm^{-1} , attributed to C–O bond stretching, while the peak between 990 and 1020 cm^{-1} is characteristic of



Figure 1. Illustrations of the most probable forms of hydrogen bonds in FPTPS (a,b) and GPTPS (c,d).



Figure 2. FT-IR spectra of TPS containing various plasticizers.

the anhydroglucose ring O–C stretch.¹² In Fig 2, a double-peak appeared in c, d and e, instead of the single peak of native starch ((a) in Fig 2) because the hydrogens of the amide (NH₂CO) groups in formamide and urea, and their blends, can form stable hydrogen bonds with the O of the anhydroglucose ring O–C since the hydrogen bond between glycerol and starch is weaker, as its peak intensity and location changed less ((b) in Fig 2). Therefore, this phenomenon should be related to the stability and intensity of newly formed hydrogen bonds between urea/formamide and the C–O groups of starch. The more stable and stronger the hydrogen bonds, then the more shifted are the correlative peaks shifted and the stronger the peaks.¹³

Thermal stability

Figure 3 presents the TGA experimental results. The forms of the mass loss curves are similar for the different TPSs. Because the boiling points of the plasticizers are above 100°C, mass loss below 100°C can be mainly ascribed to water loss. The mass loss from 100°C to the decomposition onset



Figure 3. TGA curves of TPS containing various plasticizers.

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 Table 1. The effect of the proportion of urea/formamide on the onset of decomposition and mass loss at the onset temperature in TGA experiments for TPS systems

Urea/ formamide (wt%)	30/0	20/0	15/15	10/20	0/30	Glycerol (30 wt%)
Onset tem- perature (°C)	284	288	293	290	292	289
Mass loss (%)	16.1	15.0	17.6	17.1	23.2	20.6

temperature is related to the volatilization of both water and plasticizers. Thus, the difference in the decomposition onset and mass loss at the onset temperature is mainly due to the different volatilities of the various plasticizers used. Because formamide is more volatile than glycerol and urea, the thermal stability of FPTPS is poorer than that of GPTPS and UPTPS. Considering the onset of decomposition and mass loss at the onset temperature (as shown in Table 1), mixtures of urea and formamide improve the TPS thermal stability. Because formamide is a good solvent for urea, the volatility of both formamide and urea will be reduced. The proper mixture of urea and formamide could obviously improve the TPS thermal stability.

Retrogradation

The X-ray diffraction patterns of native starch and blends stored overnight before thermoplastic processing are shown in Fig 4. After starch was blended with different plasticizers, the starch basically retained its original crystalline state. Although 20 wt% urea could not completely dissolve in 10 wt% formamide, the sharp peaks at 22.3°, related to the urea crystallinity, appear only in composites (e) and (f), while composite (d) shows no urea crystal peak. The moisture in native starch could capture the excess



Figure 4. X-ray diffraction patterns of native starch and the various blends before thermoplastic processing.



Figure 5. X-ray diffraction patterns of native starch and the various blends after thermoplastic processing (for the same systems as shown in Fig 4).



Figure 6. X-ray diffraction patterns of the various TPSs, containing different plasticizers, after storing at an RH of 50 % for 25 days.

urea. This means that urea would never separate from the TPS, which 'turned into' composite (d) in the course of storage, if moisture was not dissipated in the TPS. On the other hand, the crystallinity of native starch was maintained before thermoplastic processing (composites (b), (c) and (f)). The X-ray diffraction patterns of TPS, platicized by glycerol, formamide and urea, are shown in Fig 5. During the course of thermoplastic processing, formamide and/or urea molecules entered into the starch particles, replacing the starch intermolecular and intramolecular hydrogen bonds and destroying the crystalline structure of the native starch, just like glycerol. When these TPSs were stored at an RH of 50 % for 25 days, they showed no obvious crystalline peaks, except for GPTPS (Fig 6). As is well known, GPTPS, prone to retrogradation, shows a V_H style crystalline peak¹⁴ ((e) in Fig 6). According to van Soest *et al*,¹⁵ this V_H type is a single-helical structure 'inclusion complex', made up of amylose and glycerol. Urea and formamide can restrain retrogradation, because they form strong and more stable hydrogen bonds with starch than with glycerol, and then prevent the starch molecules from interacting and crystallizing again. Mixed plasticizers (urea and formamide) could also effectively suppress the retrogradation of TPS ((b) and (c) in Fig 6), in the same way that urea or formamide can. The crystal peaks ((c) and (d) in Fig 6) at around 22.5° were ascribed to urea crystallinity. When the ratio of formamide to urea was above 2, their extrudates with starch became stable, without any separation of urea.

Mechanical testing

The stress-strain curves of TPSs, plasticized with only urea, formamide and glycerol, or a mixture of urea and formamide, and then stored at an RH of 33 % for one week after thermoplastic processing, are shown in Fig 7. These curves showed the typical patterns of rubbery starch plastic materials as reported previously,9 except for UPTPS. The plots are 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 formamide and glycerol during thermoplastic processing, while the starch molecules were so flexible that they pack too tightly without enough space for segmental motion at room temperature. It was necessary for the starch segmental motion to employ an additional force, even up to the break point for TPS, and so UPTPS was brittle but rigid. A small quantity of formamide, substituting part of the urea, could dilute this effect and improve the toughness ((b) and (d) in Fig 7). Although both formamide and urea, could reduce the importance of hydrogen bonds in starch more than glycerol, formamide can provide TPS with enough free volume at room temperature to allow segmental motion. Therefore, FPTPS was tough, but weak ((d) in Fig 7). A mixture of formamide and urea in an appropriate proportion ((b) in Fig 7) appears to increase the elongation at break, and hence the



Figure 7. Stress-strain curves of the various TPSs containing different plasticizers.

toughness, of TPS to a greater extent than either plasticizer alone.

The effects of various mixtures of urea and formamide (maintaining a constant total content of 30 %) on the mechanical properties of TPS are shown in Fig 8. For TPS plasticized by urea alone, the peak stress was 10.6 MPa and the Young's modulus as high as 574.3 MPa, although the peak strain and energy at break were only 4.3 % and 0.22 N m, respectively. Even a small quantity of formamide (5 wt%) could significantly improve the strain and energy at break of TPS, although the stress and modulus dropped much more. For FPTPS, the stress, Young's modulus and energy at break were low, although the strain could reach 72.1 %. Figure 8 indicates that the extra formamide reinforced the TPS while the extra (unused) urea rigidified and embrittled the TPS. The most appropriate proportion was 20 wt% urea to 10 wt% formamide. This TPS showed good mechanical properties with the highest values of strain and energy at break as well as the best stress and Young's modulus. The mechanical parameters of TPS plasticized by urea (20 wt%) and formamide (10 wt%) were compared with those of TPS plasticized by glycerol (30 wt%), as shown in Table 2. The former is superior to TPS plasticized by glycerol (30 wt%) in mechanical properties, except for the yield stress and Young's modulus, after storage at an RH of 33 % for one week.



Figure 8. Effects of urea and formamide contents on the mechanical properties of urea- and/or formamide-plasticized TPSs.

Table 2. The mechanical parameters of TPS plasticized by (1) urea(20 wt%) and formamide (10 wt%) and (2) glycerol (30 wt%) alone,after storage at an RH of 33 % for one week

System	Peak	Peak	Yield	Yield	Energy	Young's
	stress	strain	stress	strain	at break	modulus
	(MPa)	(%)	(MPa)	(%)	(N m)	(MPa)
1	4.8	104.7	3.8	31.5	2.17	44.4
2	4.7	49.9	4.3	20.0	1.01	181.2



Figure 9. Effect of water content on the stress and strain of TPS plasticized by urea (20 wt%) and formamide (10 wt%).

The effect of water content on the stress and strain behavior of TPS are shown in Fig 9. The stress and strain of TPS plasticized by urea (20 wt%) and formamide (10 wt%) greatly depended on the water content. With increasing water content, the stress dropped significantly to 0.91 MPa at 25 % water content, while the strain remained above 60 % over the range of 9 to 34 % water content. Thus, tensile stress is still sensitive to moisture.

Water absorption

As shown in Fig 10, the water absorption of TPS plasticized by urea (20 wt%) and formamide (10 wt%)



Figure 10. Water content as a function of storage time for glycerol-plasticized and urea/formamide TPSs at various relative humidity levels: (a) RH, 100 %; (b) RH, 50 %; (c) RH, 0 %.

(UFPTPS) changes less than glycerol-plasticized TPS with storage time, at an RH of 100 %. In a wet environment (RH of 100 %), the water content of GPTPS changed from an initial content of 9.2 % to its equilibrium value of 49.0 %, while UFPTPS varied from 12.6 to 46.0 %. UFPTPS saved a better retention than GPTPS. In a dry environment (RH of 0 %), the equilibrium water content of GPTPS and UFPTPS was 7.2 and 9.2 %, respectively. This indicates that the water resistance of TPS was improved by introducing the mixture of urea and formamide, because urea has a better water resistance than glycerol. In addition, the difference between the initial point (ie, water content of new-made materials) of the two TPSs could be related to the difference in water loss during thermoplastic processing.

CONCLUSIONS

Mixtures of urea and formamide used as plasticizers can improve the thermal stability, mechanical properties and retrogradation of starch. Such phenomena can be explained in the following two ways. First, both urea and formamide can form more stable and stronger hydrogen bonds with the hydroxyl groups of the starch molecules than a conventional plasticizer, such as glycerol. Secondly, formamide is a good solvent for urea and so both can exist in their molecular forms in TPS. By effectively restraining the retrogradation of starch, TPS plasticized by urea (20 wt%) and formamide (10 wt%) showed a better thermal stability and water resistance. Moreover, the tensile stress, strain and energy at break reached 4.83 MPa, 104.6 % and 2.17 N m, respectively, after storage at an RH of 33 % for one week. However, the tensile stress was still sensitive to moisture.

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