

A Mixed Plasticizer for the Preparation of Thermoplastic Starch

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Abstract: In this paper, formamide was firstly used as plasticizer to prepare thermoplastic starch (TPS), which could suppress the retrogradation of TPS by X-ray diffractometry (XRD) and show a good flexibility, but was weaker than conventional glycerol-plasticized TPS (GTPS). When urea was introduced into plasticizer, both the retrogradation and mechanical properties were ameliorated. The tensile stress, strain and energy break of TPS plasticized by urea (wt. 20%) and formamide (wt. 10%), respectively, reached 4.83 MPa, 104.6 % and 2.17 N·m (Newton-meter) after it had been stored at relative humidity (RH) 30% for one week.

Keywords: Thermoplastic starch, formamide, urea, retrogradation.

Thermoplastic starch is a biodegradable material based on starch, an inexpensive and natural renewable polysaccharide, which has been widely investigated as the substitute of petroleum-derived plastics because of the increasing environment and resources problems resulted from petroleum-derived plastics. Native starch commonly exists in granule structure with about 15-45% crystallinity. During the thermoplastic process, water in starch and other plasticizers play an indispensable role¹, because the plasticizers could form the hydrogen bonds with starch, take the place of the strong action between hydroxy groups of starch molecules, and make starch plasticizing. However, the conventional GTPS was thought to tend to retrogradation after being stored for a period of time and retrogradation embrittles TPS². Urea was proved to restrain retrogradation³. Urea is a high melting solid with little internal flexibility, hence urea-plasticized TPS becomes rigid and brittle⁴ at room temperature.

Since formamide is a good solvent for urea, a combination of urea and formamide might be a better plasticizer for starch. In order to restrain the retrogradation and improve the mechanical properties of TPS, formamide and urea were used as a novel fixed plasticizer to prepare TPS.

Experimental

The plasticizers were blended (3000 rpm, 2 mins) with cornstarch (11 % moisture) by use of high-speed mixer GH-100Y (made in China), and stored overnight. When two plasticizers were used, the pre-mixture was required. The ratio of plasticizers and

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cornstarch (wt./wt.) was 30:100. The mixtures were manually fed in to the single screw plastic extruder SJ-25 (s) (screw ratio L/D=25:1). The screw speed was 20 rpm. The temperature profile along the extruder barrel was 120 , 130 , 130 , 110 (from feed zone to die). The die was a round sheet with the diameter 3 mm holes.

The IR spectra were measured with BIO-RAD FTS3000 IR spectrum scanner. The extruded TPS strips were pressured to the transparent slices, tested by the transmission method. The extruded TPS strips were pressured at 10 MPa with the flat sulfuration machine and the obtained slices were tested by a BDX3300 diffractometer for XRD. Samples 8 cm×φ3 mm in Size were operated with the Testometric AX M350-10KN materials testing machines and a crosshead speed of 10 mm/min was used for tensile testing.

Results and Discussion

In the IR spectrum of starch among three characteristic peaks between 990 and 1160 cm^{-1} , the peaks at 990 and 1020 cm^{-1} were attributed to C-O bond stretching of the anhydroglucose ring⁵. Here a double-peak appeared in **Figure 1 c, d, e** instead of the single peak of native starch (**Figure 1 a**). The hydrogen in amide (NH_2CO) group of formamide, urea and their blends could form the stable hydrogen bonds with the oxygen in anhydroglucose ring of starch, while the hydrogen bond interaction between glycerol and starch was weaker and both the peak style and situation changed a little (**Figure 1 b**).

The retrogradation of TPSs, separately plasticized by glycerol, formamide, urea and formamide/urea, was shown in **Figure 2**. The conventional GTPS stored at RH50% for 25 days presented the obvious V_H style crystal peaks at 13.81° and 21.13° (**Figure 2 e**) ascribed to starch retrogradation. According to J. J. G. Van Soest⁶, V_H -type is a single-helical structure “inclusion complex”, made up of amylose and glycerol. There was no obvious starch molecular crystal peak in the other four TPSs (**Figure 2 a, b, c, d**), because urea and formamide could form stronger and more stable hydrogen bonds with starch than glycerol, and prevent starch molecules from interacting and crystallizing again. The pointed peak at 22.48° (**Figure 2 d**), belonged to the urea crystallinity, disappeared in TPS containing formamide and urea, because formamide is a good solvent for urea. Therefore, the mixture could effectively restrain both the retrogradation of TPS and the recrystallization of urea.

TPSs, plasticized with urea, formamide, glycerol or the mixture of urea and formamide, respectively, were stored at RH30% for one week. The stress ~ strain curves were shown in **Figure 3**. The stress ~ strain diagrams of the materials showed the typical pattern of rubbery starch plastic materials reported previously², except TPS plasticized by urea. The plots (**Figure 3 b, c, d, e**) were linear at low strain and curved towards the strain axis at higher strains. TPS plasticized by 30% urea was a brittle glassy material but rigid. The addition of formamide could improve the toughness (**Figure 3 b, d**). Formamide-plasticized TPS was tough but weak (**Figure 3 d**). The mixture of formamide and urea in the appropriate proportion (**Figure 3 b**) increased the elongation at break and the toughness of TPS in greater extent than either plasticizer. Because formamide was a good solvent of urea, formamide together with moisture of native starch

could effectively prevent urea from being solidified; consequently this novel fixed plasticizer ameliorated mechanical properties of TPS with suppressing the retrogradation. The mechanical parameters of the conventional GTPS and TPS plasticized by urea (wt. 20%) and formamide (wt.10%) were compared in **Table 1**.

Figure 1 The FT-IR spectra of TPS with different plasticizers

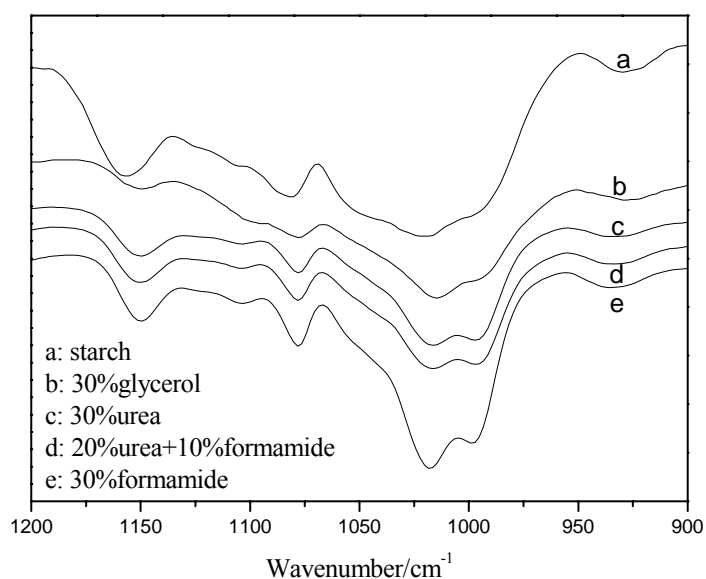


Figure 2 The diffractograms of five TPS stored at RH50% for 25 days, which were prepared by the different plasticizers

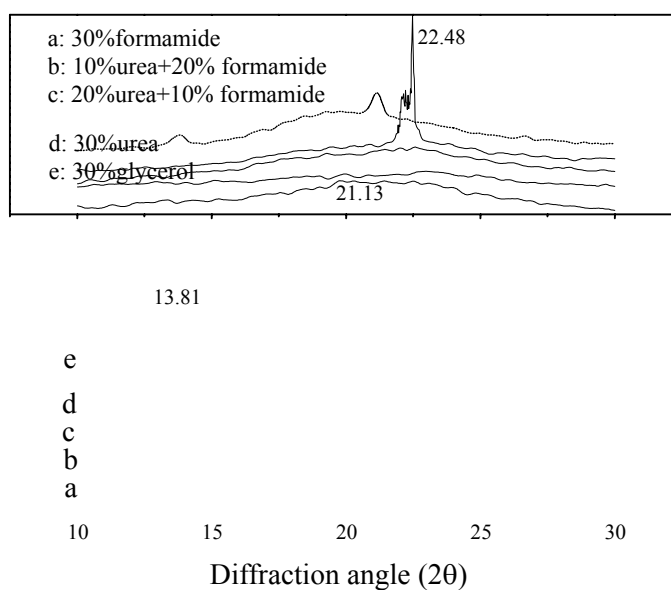
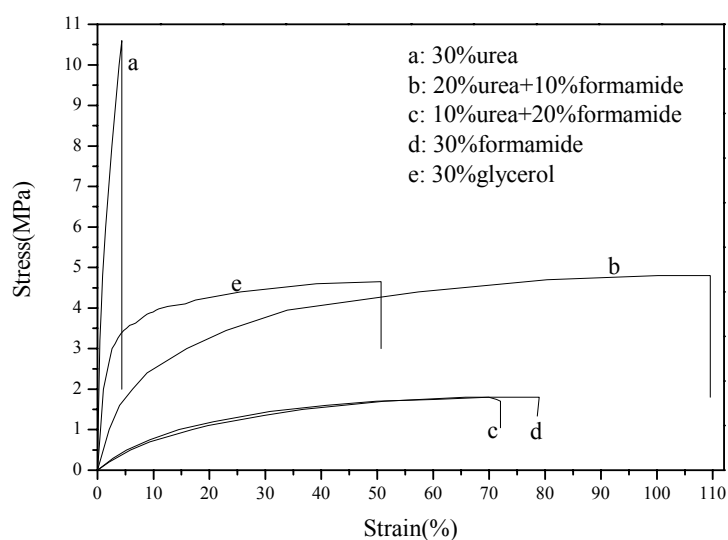


Figure 3 The stress ~ strain curves of several TPS plasticized with different plasticizers**Table 1** The mechanical parameters of TPS plasticized by urea (wt. 20%) and formamide (wt. 10%) (1) and by glycerol (wt. 30%) alone (2) stored at RH=30% for one week

	Stress Peak (MPa)	Strain Peak (%)	Stress Yield (MPa)	Strain Yield (%)	Energy Break (N·m)	Young's Modulus (MPa)
1	4.829	104.656	3.769	31.529	2.176	44.355
2	4.706	49.857	4.292	20.029	1.012	181.183

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Received 13 May, 2003