Formamide as the Plasticizer for Thermoplastic Starch

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ABSTRACT: As a novel plasticizer, formamide was tested in thermoplastic starch (TPS), in which native cornstarch granules were proved to transfer to a continuous phase by scanning electron microscope (SEM) and the hydrogen bond interaction between plasticizer and starch was proved by Fourier transform infrared (FTIR) spectroscopy. Mechanical tests showed that tensile strength and Young's modulus of formamide-plasticized TPS (FPTPS) were lower than glycerol-plasticized TPS (GPTPS) and elongation at break and energy break were higher. The effect of formamide and glycerol on the retrogradation of TPS was studied using X-ray diffractometry. Formamide could effectively restrain the starch retrogradation at three different relative humidity (RH) environments, because it could form the more stable hydrogen bonds with the starch hydroxy group than glycerol. From these results, we found that the elongation at break, energy break, and the retrogradation of TPS were ameliorated by formamide. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1769–1773, 2004

Key words: thermoplastic starch; formamide; plasticizer; retrogradation

INTRODUCTION

The improper disposition of the enormous volume of petroleum-derived plastics in the environment led to environment pollution and raised much interest in preparing the replacement from nature polymers, biodegradable and renewable resources. Currently, much research is concerned with starch, the polysaccharide of granular structure, because it is inexpensive and abundant. Starch presents two different polysaccharides: the linear (1,4)-linked α-D-glucan amylose and highly branched (1,6)-linked α-D-glucan amylopectin.[1] Commonly, amylopectin takes part in the formation of a crystalline structure, and amylose does not.[2] Natural starch usually is ~ 15–45% crystallinity. The development and production of biodegradable thermoplastic starch (TPS) is important to reduce the total amount of plastic waste. During the thermoplastic process, water contained in starch and other plasticizers plays an indispensable role, 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 display the plasticization. In most literature for thermoplastic starch, polyols as plasticizers usually were used such as glycerol,[3,4] glycol,[5] sorbitol,[6] and sugars.[7] This kind of TPS was thought to have a tendency to recrystallize (retrogradation) after being stored for a period of time and retrogradation embrittles TPS. Urea was shown to prevent retrogradation. However, it has a high melting solid with little internal flexibility and, hence, urea-plasticized TPS became rigid and brittle.[8] Therefore, for the application and development of starch materials, it is very important to discover a perfect plasticizer that imparts the flexibility and suppressed retrogradation to TPS during the aging process. Presently, there still is no research pertaining to formamide as a starch plasticizer.

In this study, we described TPS plasticized by formamide and studied the plasticization, mechanical properties, and retrogradation of this TPS. From all of the results, formamide was considered the material that could promote the plasticization of starch, improve the TPS flexibility, and restrain the retrogradation of TPS.

EXPERIMENTAL

Materials

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

Plasticization

Glycerol (150 g) and formamide (150 g) were, respectively, blended (300 rpm for 2 min) with cornstarch (500 g) by using a high-speed mixer (GH-100Y; Beijing Plastic Machinery Factory, Beijing, China) and then stored overnight. The mixtures were fed manually

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into the single screw plastic extruder SJ-25(s) (screw ratio L / D = 25 : 1; Beijing Plastic Machinery Factory). The screw speed was 20 rpm. The temperature profile along the extruder barrel was 130, 135, 140, and 120°C (from feed zone to die). The single screw extruder was equipped with a die, a round sheet with 3-mm-diameter holes.

Scanning electron microscope

The native starch and the fracture surfaces of extruded TPS strips were performed with a scanning electron microscope (SEM), Philips XL-3 (FEI, Hillsboro, OR), 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.

Fourier transform infrared spectroscopy

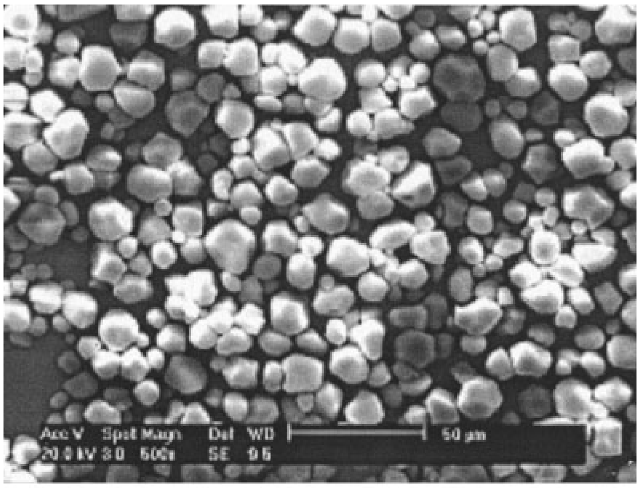
The infrared (IR) spectra were measured with a Bio-Rad FTS3000 IR spectrum scanner (Hercules, CA). The native starch powders were tested by the reflection method, and the extruded TPS strips were pressed to the transparent slices, which were tested by the transmission method.

Mechanical testing

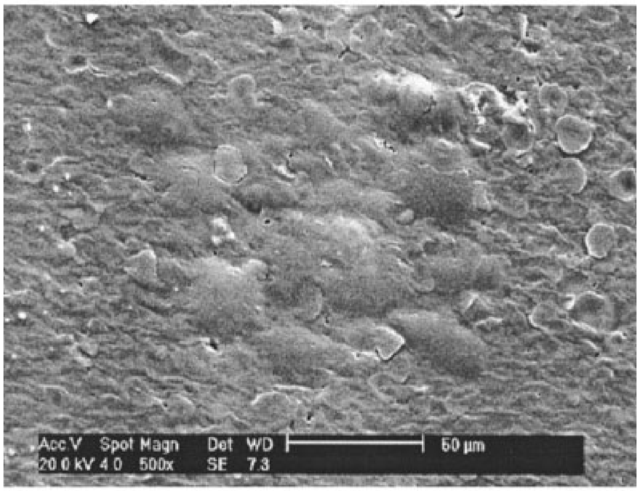
Samples 8 cm × 3 mm diameter (ϕ) in size were cut from the extruded strips. The Testometric AX M350–10KN materials testing machines (Rochdale, Lancashire, UK) operating at a crosshead speed of 10 mm/min were used for tensile testing.

X-ray diffractometry

The extruded TPS strips were pressed to the slices with a flat sulfuration machine (Beijing Plastic Machinery Factory) and the slices were placed in a sample holder for X-ray diffractometry. The native 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 BDX3300 diffractometer (Beijing University Instrument Factory, Beijing, China) operated at the CuK α-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 a 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.



(a)



(b)

Figure 1 SEM micrograph of (a) native cornstarch granules and the (B) fracture face of formamide-plasticized TPS.

RESULTS AND DISCUSSION

Plasticization

Compared with native cornstarch granules, the microcosmic morphology of the extruded TPS was shown in Figure 1. It was shown that a few percent of residual granular structure was present in the continuous formamide-plasticized TPS (FPTPS) phase. Because of the high shear and temperature conditions with the action of formamide, native cornstarch granules were molten or physically broken up into small fragments. Plasticizers were known to disrupt intermolecular and intramolecular hydrogen bonds and make the native starch plastic.

Formation of homogeneous TPS was a result of strong interactions by hydrogen bonds between starch and plasticizers. The analysis of Fourier transform IR (FTIR) spectra of the blends enables hydrogen bond interactions to be identified.[9,10] On the basis of the

TABLE I
The Relation of the Bands with Evident Changes of the Wave Number and the Corresponding Groups of Starch in the FTIR Spectrum

Corresponding group	Free, intermolecular, and intramolecular bound hydroxyl groups	C—O of C—O—H in starch	C–O of C–O–C in starch
Wave number (cm^{-1}) in native starch	3389	1156 1081	1020
Wave number (cm^{-1}) in FPTPS	3310	1150 1077	1012

harmonic oscillator model, the reduction in force constant Δf could be represented by eq. (1)[11]:

$$\Delta f = f_p - f_{np} = \frac{\mu(\nu_p^2 - \nu_{np}^2)}{4\pi^2} \quad (1)$$

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

Evident changes were found in the wave number in the bands corresponding to mobility in the group (shown in Table I). Susceptibility to the formation of intermolecular complexes within TPS induces changes in intermolecular vibrations. Figure 2 shows changes in the wave number in the region of the group vibrations related to a hydrogen bond between native starch and FPTPS. The peak frequency (3389 cm^{-1}) of native starch, ascribed to free, intermolecular, and intramolecular bound hydroxyl groups, was transferred to the lower frequency (3310 cm^{-1}). The original hydroxyl interaction in starch was weakened by the new formation of the hydrogen bond between starch and formamide. Formamide could form a more stable hydrogen bond with the hydroxyl group, so the frequency, related to the hydroxyl group, decreased a great deal in FPTPS. On the other hand, the presence of formamide decreased the wave number of the peak ascribed to the C—O stretch of C—O—H in starch at 1156 and 1081 cm^{-1} and C—O stretch of C—O—C in starch at 1020 cm^{-1}.[12] Because the new and strong hydrogen bond formation between starch and formamide took the place of the original interaction in native starch, the corresponding peak frequency was lower. Figure 2 shows that both C—O—H and C—O—C group in starch could form the hydrogen bond with the plasticizer.

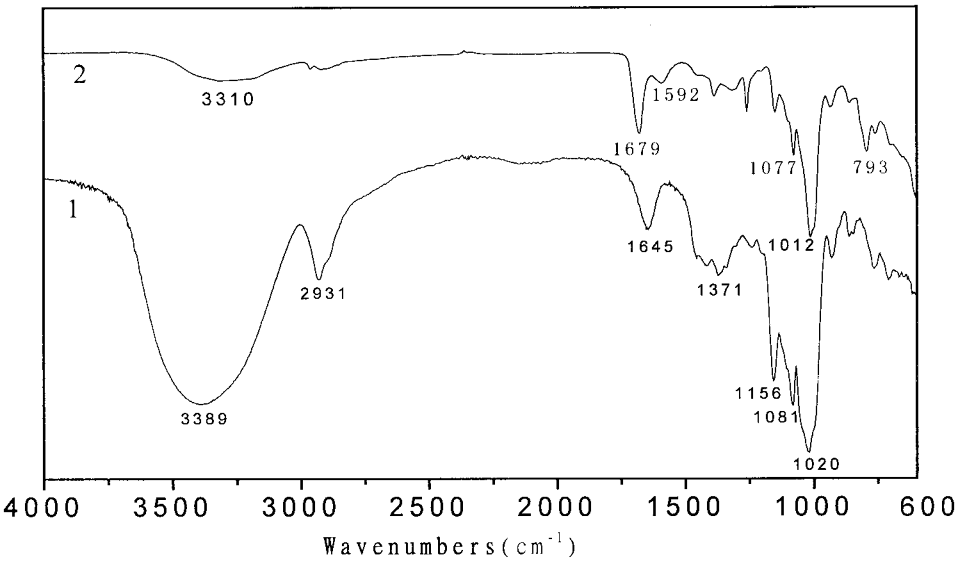


Figure 2 The FTIR spectra of native starch and formamide-plasticized TPS.

TABLE II
The Mechanical Properties of GPTPS and FPTPS

TPS	GPTPS	FPTPS
Tensile strength (MPa)	5.5	3.4
Elongation at break (%)	85	106
Energy break (N · m)	1.01	2.18
Young's modulus (MPa)	183	44

Mechanical testing

The mechanical properties of glycerol-plasticized TPS (GPTPS) and FPTPS are shown in Table II. After TPS ribbons were extruded from the single screw plastic extruder and cooled to the room temperature, mechanical properties of TPS materials were tested. Formamide could form more stronger hydrogen bond interactions with starch and weaken the interaction of starch molecules, and the slippage movement among starch molecules was facile. At the same percentage of plasticizer contents (30%), the elongation at break and energy break of FPTPS was better than one of the GPTPSs while the tensile strength and Young's modulus of FPTPS was lower. Therefore, FPTPS was more flexible than GPTPS.

Retrogradation

The X-ray diffraction patterns of TPS materials are shown in Figures 3 and 4. In the GPTPS (Figure 3 b), most crystal disappears, but a low percent of crystallinity, still observed, came from the inductive formation during the thermal process of TPS.[13] In the FPTPS (Figure 4 b), all crystallinity in the native starch (Figures 3 a and 4 a) was melted during extrusion. In this process, formamide molecules entered starch particles, replaced starch intermolecular and intramolecular hydrogen bonds, and destroyed the crystal of starch. At the same time, formamide molecules made the amylopectin more flexible than glycerol molecules, so the crystallinity, induced by remnant stress from the FPTPS process was less, and FPTPS was almost amorphous (Figure 4).

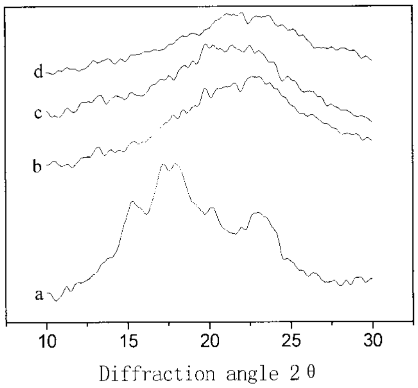


Figure 4 (a) The diffractograms of native starch and FPTPS stored at RH = 50% for 0 day (b), 25 days (c) and 70 days (d).

The effect of glycerol and formamide on the retrogradation of TPS obviously was different. The GPTPS stored at a relative humidity (RH) of 50% for 25 d (Figure 3 c) showed a greater V_H-style crystal peak because of retrogradation of starch as well as a GPTPS stored at an RH of 50% for 70 d (Figure 3 d). According to VanSoest,[14] the V_H type is a single-helical structure "inclusion complex" made up of amylose and glycerol. In the presence of formamide, X-ray diffraction showed that no crystal state could be observed in FPTPS stored at an RH of 50% for 25 d and 70 d (Figure 4 c and d).

Under extreme dry conditions (RH = 0), the GPTPS stored for 70 d showed an obvious V_H-type crystal peak (Figure 5), whereas FPTPS showed nothing under the same storage conditions. At high humidity (RH = 100%), the GPTPS stored for 70 d represented the mixture of V_H-type and A-style crystal (Figure 6). Because the high water content could dilute the action between starch and glycerol, starch molecules could

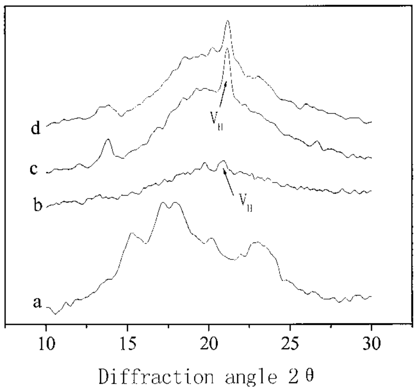


Figure 3 The diffractograms of (a) native starch and GPTPS stored at an RH of 50% for (b) 0 d, (c) 25 d, and (d) 70 d.

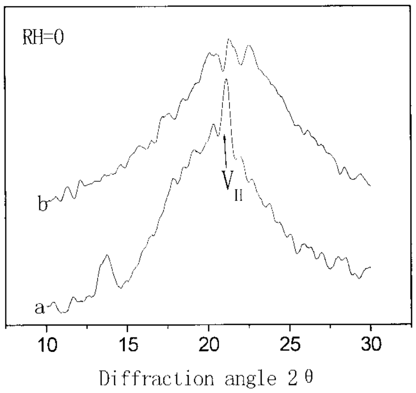


Figure 5 The diffractograms of (a) GPTPS and (b) FPTPS stored at an RH of 0 for 70 d.

form A-style crystal with starch molecules and form the V_H-type crystal with glycerol again (Figure 6 a), while starch molecules could not form the V_H-type crystal with formamide and A-style crystal was not very clear (Figure 6 b). The hydrogen bond interaction between formamide and starch was so strong that the additional water could not obviously weaken this interaction.

In this recrystallization of TPS stored at different humidities, formamide could effectively inhibit hydrogen bond reformation among starch molecules and, consequently, prevented the retrogradation of TPS. The suppressive effect of formamide and glycerol on the retrogradation of TPS should be related to their hydrogen bond–forming abilities with starch.

To estimate the difference in the hydrogen bond–forming abilities between formamide and glycerol, we simplified the voluminous hydrogen bond possibility. For example, three-center H-bond and nitrogen as an H-bond donor (the electronegativity of nitrogen is weaker than oxygen) were not considered here. The representative styles of the hydrogen bonds in both FPTPS and GPTPS are shown in Figure 7. When the acceptor of hydrogen bonds was H of the OH group in starch, as the electron donor, O of the carbonyl group in formamide (Figure 7 a) had more electronegativity than O of the hydroxy group in glycerol (Figure 7 c), because the electron-donating effect of carbonyl double bonds made the electron cloud density of O in the carbonyl group greater. When the donor of hydrogen bonds was O of the OH group in starch, H of the amino group in formamide (Figure 7 b), as the electron acceptor, had less electronegativity than H of the hydroxy group in glycerol (Figure 7 d), because the N—C═O group with p-π conjugate structure exposed the H connected with N in formamide. Consequently, the order of the hydrogen bond–forming abilities shown in Figure 7 is as follows: (a) > (c) and (b) > (d).

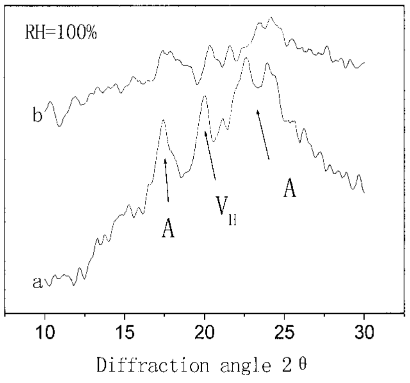


Figure 6 The diffractograms of (a) GPTPS and (b) FPTPS stored at an RH of 100% for 70 d.

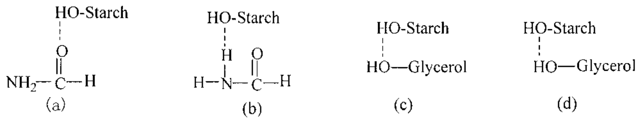


Figure 7 The representative styles of the hydrogen bonds in (a and b) FPTPS and (c and d) GPTPS.

Therefore, formamide could form the more stable hydrogen bonds with starch than with glycerol. In other words, the hydrogen bond interaction of starch molecules was weaker in FPTPS than in GPTPS, and the recrystallization of starch molecules was more difficult to form. In fact, the strong hydrogen bonds between the formamide and hydroxy groups of starch made formamide suppress the retrogradation of TPS.

CONCLUSION

We reported that formamide was a favorable plasticizer for starch plasticization, proved by SEM and FTIR methods. Mechanical characters revealed that in contrast with GPTPS, tensile strength and Young's modulus of FPTPS were lower while elongation at break and energy break were higher. On the other hand, formamide could suppress the retrogradation of TPS at three different environments (RH = 0, 50, and 100%). The newly formed hydrogen bonds between formamide and starch hydroxyl, which are more stable, prevented starch hydroxyls from resuming the hydrogen bond action of starch during the aging process. Therefore, as a novel plasticizer, formamide is worth researching in detail and will be helpful for extending TPS application scopes.

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