Available online at www.sciencedirect.com
SCIENCE DIRECT®

Carbohydrate Polymers 57 (2004) 197–203

Carbohydrate Polymers
www.elsevier.com/locate/carbpol

The plastcizers containing amide groups for thermoplastic starch

Xiaofei Ma, Jiugao Yu*

School of Science, Tianjin University, Tianjin 300072, China

Received 29 March 2003; revised 27 March 2004; accepted 21 April 2004

Abstract

Including formamide, acetamide and urea, several plasticizers containing amide groups for thermoplastic starch (TPS) were studied with the reference of glycerol in this paper. The effects of water contents on mechanical properties of TPS showed that formamide-plasticized TPS (FPTPS) had a good flexibility at the wide scope of water contents, and the strain of UPTPS increased up to 65% at high water content (42%). Fourier Transform infrared (FT-IR) spectroscopy showed that a small percent of urea could react with starch at the given TPS processing conditions. The other plasticizers could not react with starch. The order of the hydrogen bond-forming abilities with starch was urea > formamide > acetamide > polyols, confirmed by B3LYP chemical computation. The hydrogen-bonding interaction in 1:1 complexes formed between plasticizers (urea, formamide, acetamide or glycerol) and starch were respectively 14.167, 13.795, 13.698 and 12.939 kcal/mol. Glycerol-plasticized TPS, FPTPS, acetamamide-plasticized TPS and urea-plasticized TPS were tested at three typical humidities using X-ray diffractometry. Urea and formamide could effectively restrain the retrogradation of TPS, and acetamide could not increase re-crystalline of original APTPS. The properties of TPS mainly relied on the hydrogen bond-forming abilities between plasticizers and starch molecules.

Keywords: Thermoplastic starch; Formamide; Acetamide; Urea; Retrogradation

1. 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, the biodegradable and renewable resources. Currently much research concerns on starch, the polysaccharide of granular structure, for it is inexpensive and abundant. The development and production of biodegradable thermoplastic starch (TPS) is considered it important to reduce the total amount of plastic waste. Starch presents two different polysaccharides: the linear (1,4)-linked α-D-glucan amylose and highly (1,6)-branched α-D-glucan amylopectin. Nature starch is about 15–45% crystallinity. During the thermoplastic process, water contained in starch and other plasticizers play 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 hydroxy groups of starch molecules, and make starch display the plasticization. In most literatures for TPS, polyols as plasticizers were usually used such as glycerol (Fishman, Coffin, Konstance, & Onwulata, 2000; Forssell, Mikkilä, Moates, & Parker, 1998; Liu, Yi, & Feng, 2001), glycol (Yu, Gao, & Lin, 1996), sorbitol (Wang & Shogren, 2000) and sugars (Barret, Kaletunc, Rosenburg, & Breslauer, 1995). This kind of TPS was thought to tend to re-crystallization (retrogradation) after being stored for a period of time and retrogradation embrittles TPS (Van Soest & Knooren, 1996). Urea was shown to prevent retrogradation. It is, however, a high melting solid with little internal flexibility and hence urea-plasticized TPS becomes rigid and brittle (Thomas and Richard, 1997). So it is very important for the application and development of starch materials to discover a perfect plasticizer, which imparts the flexibility and suppressed retrogradation to TPS during the aging time. By now, the research pertaining to formamide and acetamide as plasticizers for TPS is still in blank.

In this paper, we regarded glycerol-plasticized TPS as the contrast, described TPS plasticized by formamide, acetamide and urea, and studied the plasticization, mechanical properties and retrogradation of these TPSs. Amide groups

---

* Corresponding author. Tel.: +860-2227406144; fax: +860-2227403475.

E-mail address: makong2001@hotmail.com (J. Yu).

0144-8617/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2004.04.012

were advantageous to suppressing the retrogradation of TPS. The results illuminated that the properties of TPSs mainly relied on the hydrogen bond-forming abilities between plasticizers and starch molecules.

2. Experimental

2.1. Materials

Cornstarch (11% moisture) was obtained from Langfang Starch Company (Langfang, Heibei, China). The plasticizers, glycerol, acetamide, formamide, anhydrous glucose and urea, were purchased from Tianjin Chemical Reagent Factory (Tianjin, China). The plasticizers were analytical reagents.

2.2. Plasticization

The plasticizers were blended (3000 rpm, 2 min) with cornstarch by use of High Speed Mixer GH-100Y (made in China), and then stored overnight. When two plasticizers were used together, another step for the pre-mixture of them was required. The ratio of plasticizers and cornstarch (w/w) was 30:100. Glycerol-plasticized TPS (GPTPS), Glycerol/-glucose plasticized TPS, urea-plasticized TPS (UPTPS), acetamide-plasticized TPS (APTPS), formamide-plasticized TPS (FPTPS) and formamide/acetamide-plasticized TPS (F-APTPS) were prepared as following: The mixtures were manually fed in to the single screw Plastic extruder SJ-25(s) (Screw Ratio L/D = 25:1, made in China). The screw speed was 20 rpm. The temperature profile along the extruder barrel was 130, 135, 140, 120 °C (from feed zone to die). The die was a round sheet with the diameter 3 mm holes.

2.3. Mechanical testing

Samples 8 cm × Φ3 mm in Size were cut from the extruded strips. An electronic Universal Testing Machine WD-5 (made in China) operated and a crosshead speed of 10 mm/min was used for tensile testing. The average of five bars was recoded for every sample.

2.4. Chemical computation

The used theoretical method was the hydride density functional method B3LYP. And all calculations were performed using the Gaussian98.

2.5. Fourier transform infrared (FT-IR) spectroscopy

The IR spectra were measured with BIO-RAD FTS3000 IR Spectrum Scanner. The extruded TPS strips firstly were ground to powders, washed with ethanol: water (70:30,V/V) to remove the residual plasticizers, then dried in an oven at 100 °C for 3 h. The obtained powders and the native starch powders were tested by the reflection method. In processing of APTPS and FPTPA except UPTPS, no obvious reaction evidence was reflected in IR spectra, which were not shown in this paper.

2.6. Storage conditions and water contents

In order to analyse the effect of environmental humidity on tensile properties and TPS retrogradation, the bars for mechanical testing were stored in closed chambers over several materials at 20 °C for 5 or 10days. The materials used were dried silica gel, substantive 55.01% H_2SO_4 solution, substantive 35.64% $CaCl_2$ solution, NaCl saturated solution and distilled water, providing relative humidities (RH) 0, 25, 50, 75 and 100%, respectively. The slices for X-ray diffractometry were stored at 0, 50 and 100% RH. Every several days the slices were tested.

Water contents were determined gravimetrically by drying small pieces of TPS at 105 °C overnight. At this condition, evaporation of glycerol and formamide was negligible.

2.7. X-ray diffractometry

The extruded TPS strips were pressed into the slices with the Flat Sulfuration Machine at 10 MPa. After some storage time at several RHs, the slices were placed in a sample holder for X-ray diffractometry. The native cornstarch 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 Kαwavelength 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.

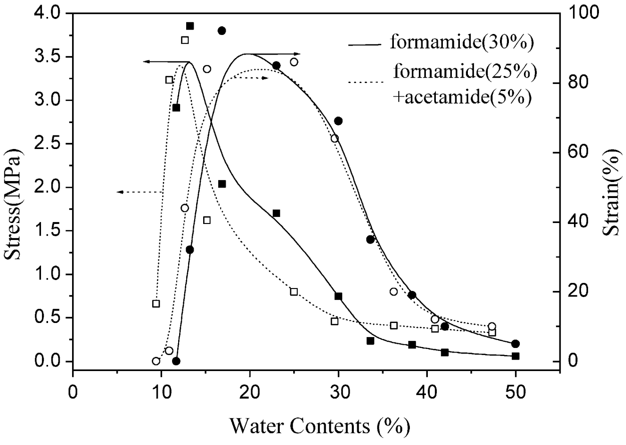


Fig. 1. The effect of water contents on the retrogradation of FPTPS and F-APTPS.

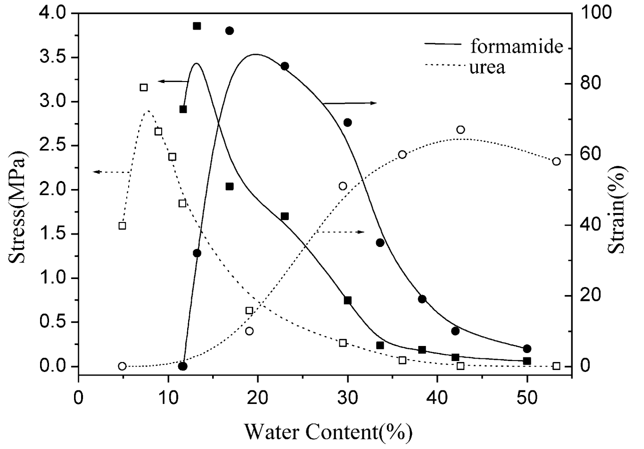


Fig. 2. The effect of water contents on the retrogradation of FPTPS and UPTPS.

3. Results and discussion

3.1. Mechanical properties

The strips were conditioned at different RHs. Changes in the environmental humidity greatly affected the water contents of the strips, which in return, induced large changes in failure stress and strain. For both FPTPS and F-APTPS strips (Fig. 1), with the increasing of water contents the tendency of the stress was similar to each other, because formamide and acetamide were the homologue. Each of four curves in Fig. 1 had a peak at the low and intermidate water contents (10–20%). In excess or shortage of water contents, FPTPS and F-APTPS strips would lose the strength and elongation. The low stress and elasticity at high water contents were explained in terms of a weakening of the interactions between the starch molecules (Van Soest, Bense, de Wit, & Vilegenthart, 1996). And at the lack of water the newly formed hydrogen bonds of starch could embrittle TPS and then reduced the strength.

FPTPS and F-APTPS had the similar mechanical properties, but APTPS had a poor failure stress and strain (not shown in Fig. 1). The re-crystallization of acetamide, a solid at the room temperature, would embrittle the TPS. But if a small quantity of acetamide were dissolved into formamide, the mixtures were together used as the plasticizer for TPS, then the mechanical properties of obtained TPS would be still acceptable. Understandably, acetamide dissolved in formamide still could prevent the interaction of starch molecules at the stored temperature. However, this effect of acetamide was weaker for methylic steric hidrance than formamide.

As shown in Fig. 2, the stress of UPTPS was below one of FPTPS at the same of water contents, while the curves of the strain were so different that the peak situation for UPTPS was deferred to about 42% water content. Such as acetamide, urea was also a high melting solid, but urea could form more stable hydrogen bonds with starch molecules than acetamide because of the double amino groups of urea. Shogen, Swanson, and Thompson (1992) considered that about 0.25 g of urea bounded to per g of starch in TPS composed of urea and starch. The unbound urea, which embrittled UPTPS at the low water contents, could gradually dissolve into the additional water with the increasing of water contents, and then the bound urea could also dissolve, therefore, the strain of UPTPS increased up to 65% at high water content (42%).

TPS, plasticied by acetamide alone, was fragile and acetamide was prone to separate out from TPS, so the mechanical properties of APTPS were not shown in this paper.

3.2. H-bonding interaction between the various plasticizers and starch

To estimate the difference in the hydrogen bond-forming abilities among formamide, acetamide, urea and polyols (such as, glycerol, glycol, sorbitol, sugars, and so on), we regarded acetamide and glycerol as an example. The styles of the most possible hydrogen bonds in both APTPS and GPTPS were shown in Fig. 3. When the acceptor of hydrogen bonds was H in OH group in starch, as the electron donor, O in carbonyl group of acetamide (a in Fig. 3) had more electronegativity than O in hydroxy group of glycerol (c in Fig. 3), for the electron donating effect of carbonyl double bonds made electron cloud density of O in carbonyl group greater. When the donor of hydrogen bonds was O in OH group in starch, H in amino group of acetamide (b in Fig. 3), the electron acceptor, had less electronegativity than H in hydroxy group of glycerol (d in Fig. 3), because the amide group bared H connected with N in acetamide. So the order of the hydrogen bond-forming abilities as following: (a) > (c) and (b) > (d). Each urea molecular has double amino groups, so it could form more stable hydrogen bonds

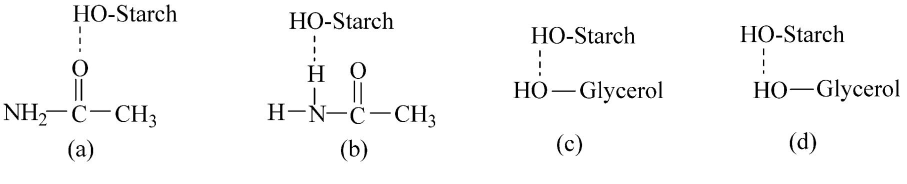


Fig. 3. The styles of the most possible hydrogen bonds in both APTPS (a,b) and GPTPS (c,d).

Table 1
The hydrogen bond energy of complexe between starch and plasticizers (1:1) (Estarch = −765.63070082 (a.u), ΔE/a.u., 1 a.u. = 27.21 eV = 627.51 kcal/mol)

Complex	$E_{\text{plasticizer}}$ (a.u.)	$E_{\text{comp.}}$ (a.u.)	Hydrogen bond (ΔE)		
			(a.u.)	(eV)	(kcal/mol)
G/S	−344.71413615	−1110.36545618	0.02062003	0.561	12.939
A/S	−208.89730025	−974.50617194	0.02182913	0.594	13.698
F/S	−169.86381140	−935.51649688	0.02198466	0.598	13.795
U/S	−225.22596575	−990.87924372	0.02257715	0.614	14.167

with starch than formamide, while acetamide could form less strong hydrogen bonds with starch than formamide because of methylic steric hidrance. Therefore, the order of the hydrogen bond-forming abilities with starch as following: urea > formamide > acetamide > polyols.

The calculated structures of urea, formamide, glycerol and starch (glucose unit model with methyl ends) using B3LYP (the hybrid density functional methods) were gained. At B3LYP employed, the hydrogen bonding of 1:1 complexes formed between plasticizers (urea, formamide or glycerol) and starch were investigated.

Interaction energies were calculated for the plasticizer-starch hydrogen bond by taking the energy difference between the fragments and the complex.

$$E_{(\text{interaction})} = E_{(\text{starch})} + E_{(\text{plasticizer})} - E_{(\text{comp.})}$$

where $E_{(\text{starch})}$, $E_{(\text{plasticizer})}$ and $E_{(\text{comp.})}$ were the electronic energies of starch, plasticizer and the complex, respectively. The more the value of $E_{(\text{interaction})}$, the more stable the hydrogen bond was. The results were listed in Table 1. $E_{(\text{interaction})}$ between starch and the plasticizers were among 0.020 (0.56 eV) ~ 0.023 (0.62 eV), respectively,

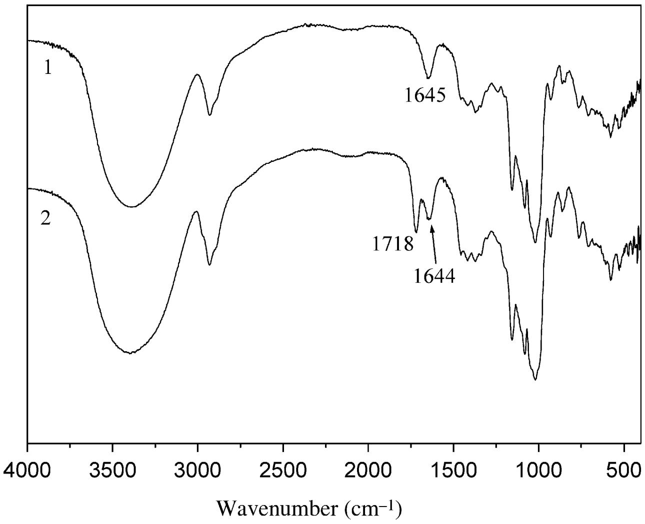


Fig. 4. The FT-IR spectra of native starch (1) and UPTPS powders (2).

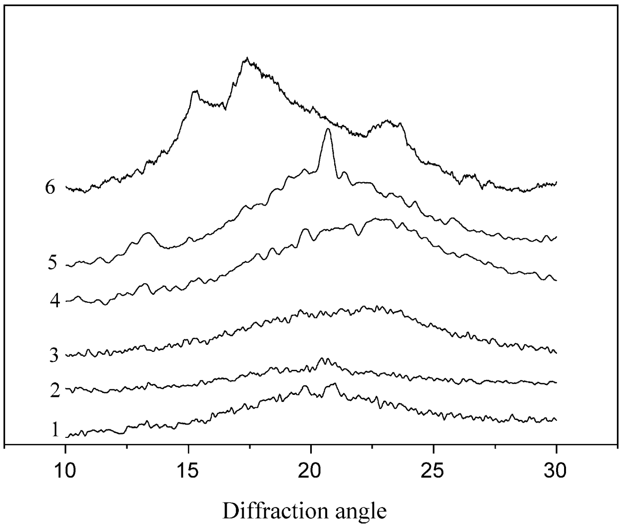


Fig. 5. The diffractograms of native cornstarch and the original TPS plasticized by several different plasticizers 1. GPTPS 2. Glycerol/glucose (20/10%) plasticized TPS 3. UPTPS. 4. FPTPS 5. APTPS 6. Native Cornstarch.

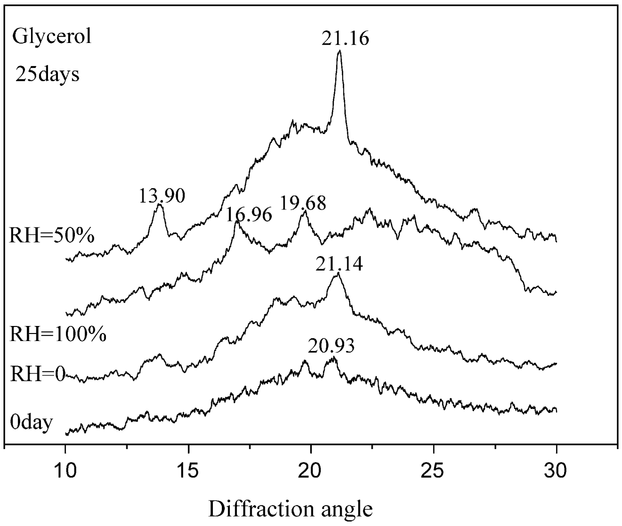
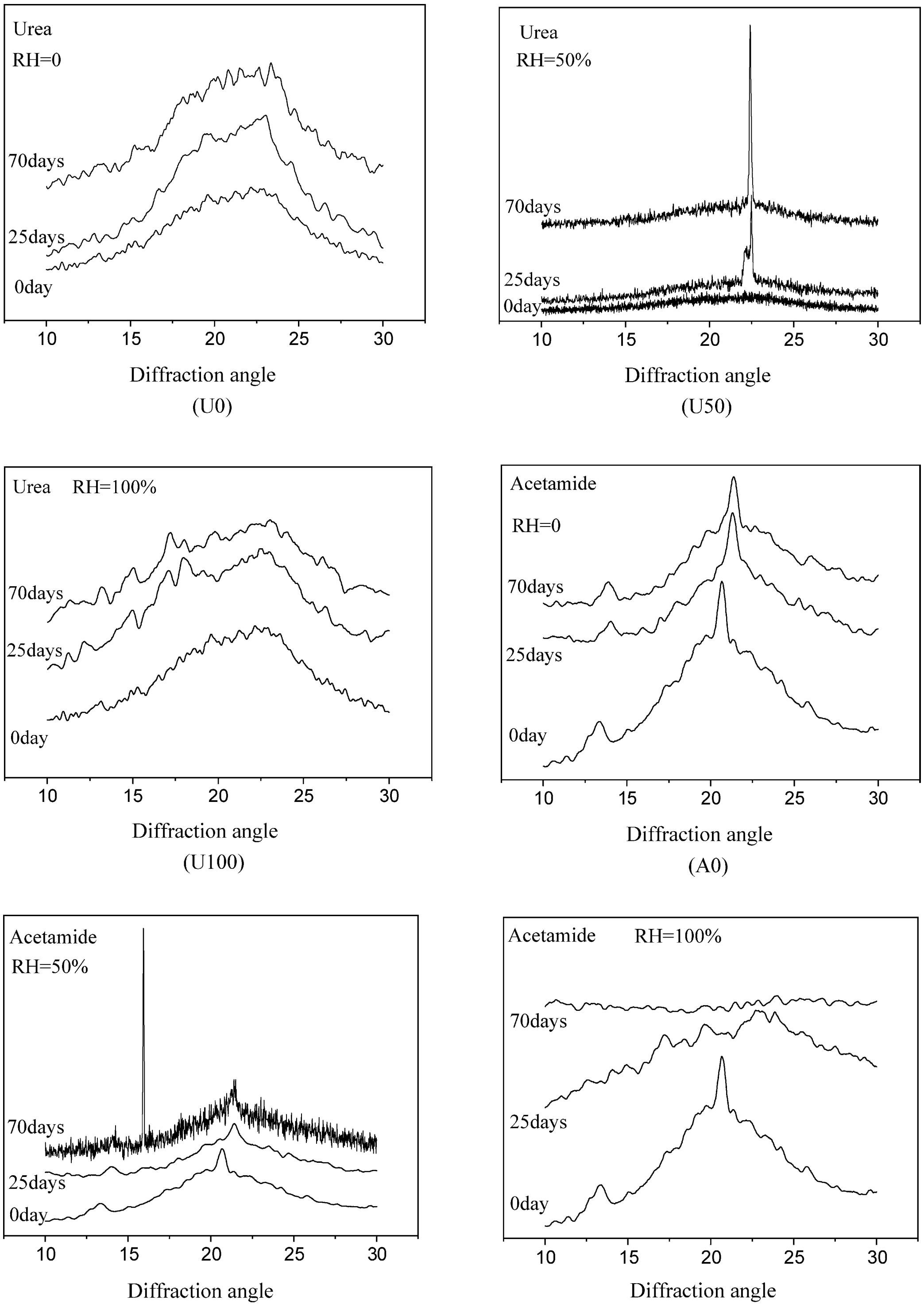


Fig. 6. The X-ray diffractograms about the retrogradation of GPTPS stored at RH = 0, 50 and 100% for 25 days.

which belonged to a kind of weak intermolecular interaction and was between covalent bond energy (~3.0 eV) and van der Waals' interaction energy (~0.1 eV). (Mao et al., 2000)

The order of hydrogen-bonding energy between plasticizer and starch was urea–starch > formamide–starch > acetamide–starch > glycerol–starch, and the hydrogen-bonding energy were, respectively, 14.167, 13.795, 13.698 and 12.939 kcal/mol.

Therefore, in TPS the order of hydrogen-bonding interaction between starch and the plasticizers was estimated as following: urea > formamide > acetamide > polyols.



(U0) (U50)

(U100) (A0)

(A50) (A100)

Fig. 7. The X-ray diffractograms about the retrogradation of UPTPS, APTPS and FPTPS stored at RH = 0, 50 and 100% for 25 and 70 days.

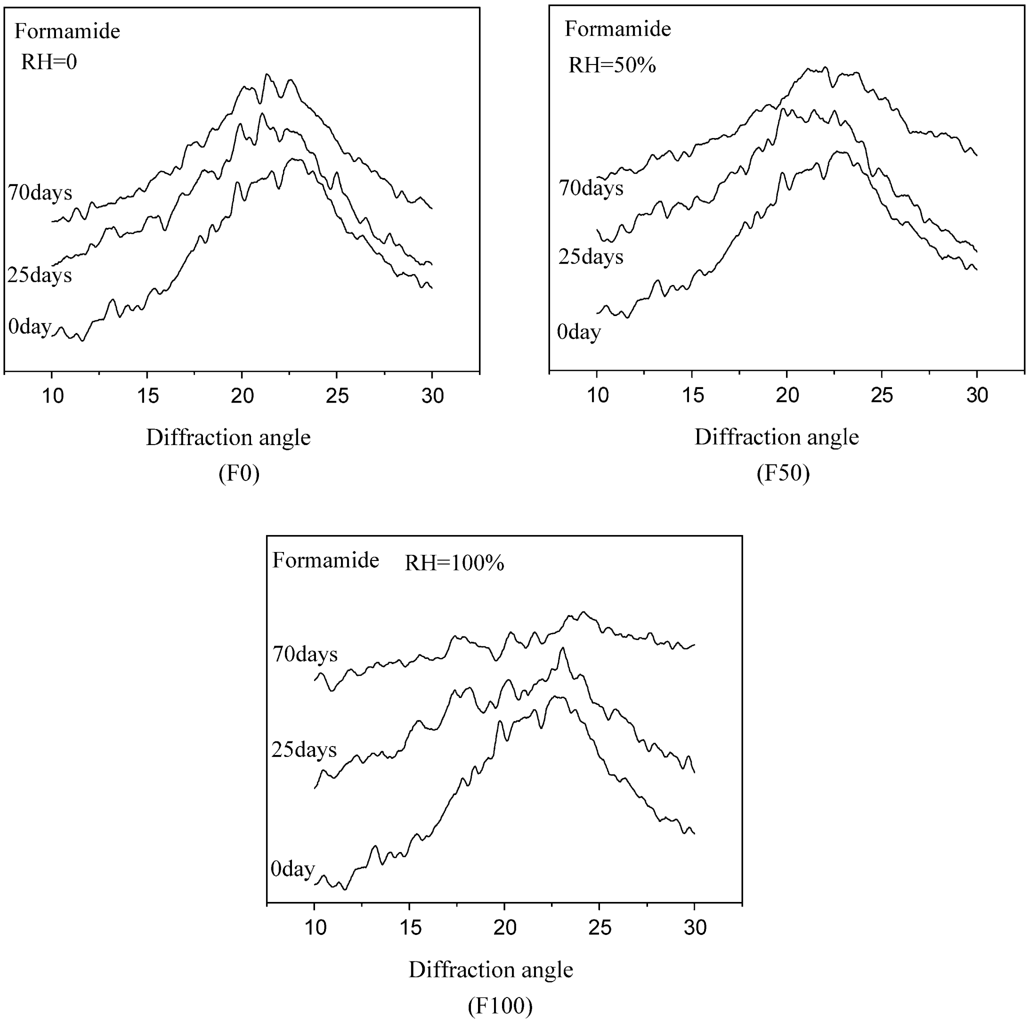
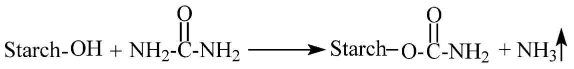


Fig. 7 (*continued*)

3.3. Chemical reaction during the processing

Fig. 4 showed the FT-IR spectra of native starch and UPTPS powders. The characteristic peak occurs at 1645 cm^{-1}, which Fang, Fowler, Tomkinson, & Hill (2002) believed to be feature of tightly bound water present in the starch. An extremely broad band due to hydrogen bonded hydroxyl groups (O–H) appears at its most intense at 3389 cm^{-1} that was attributed to the complex vibrational stretches associated with free, inter- and intra-molecular bound hydroxyl groups. For UPTPS powders, a new peak at 1718 cm^{-1} was characteristic of ester group, affected by the nearby amido group. But the broad band at 3389 cm^{-1} did not visibly changed, so it meant that only a small part starch reacted with urea during the processing. The reaction equation was as follow:



$$\text{Starch-OH} + NH_2\text{-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-}NH_2 \longrightarrow \text{Starch-O-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-}NH_2 + NH_3\uparrow$$

However, the reactions of starch and plasticizers were not found in the processing of FPTPS and APTPS. This indicated that the action between urea and starch hydroxyl group was so strong that a small proportional covalent bonds took the place of hydrogen bonds in the processing of UPTPS.

3.4. Retrogradation

The X-ray diffraction patterns of native cornstarch and original TPS (newly prepared) materials were shown in Fig. 5. Compared with native cornstarch (line 6 in Fig. 5), the crystal behavior of TPS plasticized by several different plasticizers changed much. In the processing, plasticizer molecules entered into starch particles, and then should replaced starch intermolecular and intramolecular hydrogen bonds and destructed the crystallinity of starch. Therefore, native cornstarch was the A-style crystallinity, while there were no obvious crystals in TPS except APTPS (line 5 in Fig. 5). The V_H-style crystallinity showed in original APTPS (line 5 in Fig. 5), from the inductive formation during the thermal process, was different from A-style crystallinity in native cornstarch. As a plasticizer, acetamide firstly destroyed the native cornstarch crystallinity, and then formed the new one. But when APTPS was cooled to the room temperature, starch molecules could form the V-style crystallinity with the solid acetamide, separated out. Although glucose and urea also were solid at room temperature, Glycerol/glucose plasticized TPS (line2 in Fig. 5) and UPTPS (line3 in Fig. 5) were amorphous, for urea molecules could form more stable hydrogen bonds with starch while glucose could exist in glycerol.

The retrogradation of TPSs, separately plasticized by acetamide, formamide, urea and glycerol, was reflected in Figs. 6 and 7. GPTPSs, whose crystallinitys at three typical RHs were clear in Fig. 6, were involved as the contrast. The X-ray diffractograms of UPTPS were shown in Fig. 7 U (0), U (50) and U (100), where there were no obvious starch molecular crystal peak after UPTPSs were stored at RH = 0, 50 and 100% for 25 or 70 days. The pointed peaks in U (50) at 22.3° should belong to the urea crystallinity at the surface of UPTPS sample. At the most situations for APTPSs (Fig. 7A (0), A (50) and A (100)), the V_H-style was obtained except one stored at RH = 100%. In APTPS at RH = 50% for 70 days, the additional pointed peak was acetamide crystallinity peak at 15.94°. FPTPSs hardly had the obvious crystallinity peak in Fig. 7 F (0), F (50) and F (100). It meant that urea and formamide could effectively suppress the retrogradation of TPS.

The effect of water on the retrogradation was the significant differences among GPTPS, UPTPS, APTPS and FPTPS. Because of the strong hydrogen bond-forming abilities with starch for urea and formamide, the water little impacted on retrogradation of UPTPS and FPTPS. At the high water contents, the retrogradation of TPS was obviously restrained except GPTPS (RH = 100% in Fig. 6). Even APTPS stored at RH = 100% for 25 and 70 days absolutely lost the original crystallinity, for the absorbed water dissolving the separated acetamide, made it again exert the action of plasticizer. At the low and intermediate water contents, the crystallinity relevant to starch, which was formed during the processing, approximately kept steady for APTPS stored at RH = 0 and 50% for 25 and 70 days (Fig. 7A (0) and A (50)), while GPTPS stored at RH = 0 and 50% for 25 days (Fig. 6) had greater crystallinity than original GPTPS, but the V_H-style was undiversified. It meant that acetamide more effectively restrained the retrogradation of TPS than glycerol. On the other hand, the properly additional water (RH from 0 to 50% in Fig. 6) was of advantage to the re-crystallization for GPTPS.

The retrogradation of TPS was greatly dependent on the hydrogen bond-forming abilities of plasticizers with starch molecules. The stronger the hydrogen bond between starch and the plasticizer was, the more difficult starch re-crystalline was during the storage time of TPS. And Amide groups were advantageous to suppressing the retrogradation of TPS.

4. Conclusion

At water contents of 15–35%, FPTPS and F-APTPS had good flexibility, while UPTPS had at above 26% water contents with the poor stress. Urea and formamide could effectively suppress the retrogradation of TPS, and acetamide could not increase re-crystalline of original APTPS. Amide groups were advantageous to suppressing the retrogradation of TPS. Mechanical properties and the retrogradation of TPS mainly relied on the hydrogen bond-forming abilities between plasticizers and starch molecules. The order of the hydrogen bond-forming abilities with starch as following: urea > formamide > acetamide > polyols.

References

Barret, A., Kaletunc, G., Rosenburg, S., & Breslauer, K. (1995). Effect of sucrose on the structure, mechanical strength and thermal properties of corn extrudates. *Carbohydrate Polymers*, *26*, 261–269.

Fang, J. M., Fowler, P. A., Tomkinson, J., & Hill, C. A. S. (2002). The preparation and characterisation of a series of chemically modified potato starches. *Carbohydrate Polymer*, *47*, 245–252.

Fishman, M., Coffin, D. R., Konstance, R. P., & Onwulata, C. I. (2000). Extrusion of pectin/starch blends plasticized with glycerol. *Carbohydrate Polymer*, *41*, 317–325.

Forssell, P., Mikkilä, J. M., Moates, G. K., & Parker, R. (1998). Phase and glass transition behavior of concentrated barley starch–glycerol–water mixtures, a model for thermoplastic starch. *Carbohydrate Polymer*, *34*, 275–282.

Hulleman, S. H., Janssen, F. H. P., & Feil, H. (1998). The role of water during plasticization of native starches. *Polymer*, *39*, 2043–2048.

Liu, Z., Yi, X. S., & Feng, Y. (2001). Effects of glycerin and glycerol monstearate on performance of thermoplastic starch. *Journal of Materials Science*, *36*, 1809–1815.

Mao, S. C., Yu, X. Y., Shen, Y., & Zheng, K. (2000). Ab initio study on the H-bonding complexes formed from phenol and a series of amides. *Chinese Journal of Organic Chemistry*, *20*, 243–247.

Shogren, R., Swanson, C. L., & Thompson, A. R. (1992). Extrudates of cornstarch with urea and glycols: structure/mechanical property relations. *Starch/Stärke*, *44*, 335–338.

Van Soest, J. J. G., Bense, K., de Wit, D., & Vilegenthart, J. F. G. (1996). The influences of starch molecular mass on the properties of extruded thermoplastic starch. *Polymer*, *37*, 3543–3552.

Van Soest, J. J. G., & Knooren, N. (1996). Influence of glycerol and water content on the structure and properties of extruded starch plastic sheets during aging. *Journal of Applied Polymer Science*, *64*, 1411–1422.

Wang, L., Shogren, R., & Carriere, C. (2000). Preparation and properties of thermoplastic starch–polyester laminate sheets by coextrusion. *Polymer Engineering and Science*, *40*, 499–506.

Yu, J., Gao, J., & Lin, T. (1996). Biodegradable thermoplastic starch. *Journal of Applied Polymer Science*, *62*, 1491–1494.