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The Effects of Citric Acid on the Properties of Thermoplastic Starch Plasticized by Glycerol

The effects of citric acid on the properties of glycerol-plasticized thermoplastic starch (GPTPS) were studied. In the presence of citric acid and glycerol, native cornstarch granules are transferred to a continuous phase as shown by scanning electron microscopy (SEM). As shown by thermogravimetric analysis (TGA), the improvement in thermal stability confirms that the adhesion between citric acid, glycerol, water and starch in TPS was enhanced with the addition of citric acid. It was proven by Fourier transform infrared (FTIR) spectroscopy that citric acid can form stronger hydrogen-bond interactions with starch than glycerol. Both FTIR spectroscopy and X-ray diffractometry of citric acid-modified GPTPS (CATPS) revealed that citric acid can effectively inhibit starch re-crystallization (i.e. retrogradation), because of the strong hydrogen-bond interaction between citric acid and starch. Rheology studies revealed that citric acid can obviously decrease the shear viscosity and improve the fluidity of TPS. Citric acid can also improve the elongation of GPTPS and ameliorate the water resistance of GPTPS at high relative humidities, but decreased the tensile stress.

Keywords: Thermoplastic starch; Citric acid; Glycerol; Retrogradation

1 Introduction

Much effort 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 from a great variety of crops, was one of the promising raw materials for the production of biodegradable plastics [1]. However, because of the strong intermolecular and intramolecular hydrogen bonds in starch, native starch is not a true thermoplastic. But in the presence of plasticizers (e.g. water [2], glycerol [3], etc.) at high temperatures (90–180 °C) and under shear, starch readily melts and flows, allowing for its use as an injection, extrusion or blow molding material, similar to most conventional synthetic thermoplastic polymers [4].

In most reported studies on thermoplastic starch (TPS), polyols were used as plasticizers, for example glycerol [5, 6], glycol [7, 8], sorbitol [9] and sugars [10]. This type of TPS was thought to tend to re-crystallization (retrogradation) after being stored for a period of time, which results in embrittlement. Some plasticizers containing amide groups, such as formamide [11, 12], acetamide [11], urea [11] or a formamide/urea [13] mixture were used to prepare TPS with good resistance to retrogradation. However, these plasticizers containing amide groups are possibly harmful to health. Compared to glycerol-plasticized TPS (GPTPS), use of TPS plasticized by these amides would be restricted in many applications such as fast food service-ware (cups, cutlery, plates, straws, etc.), food packaging, hygiene (e.g. diapers) and so on.

The objectives of this primary research were to study the properties of citric acid-modified GPTPS (CATPS) in order to improve the resistance of TPS to retrogradation, its thermal stability, rheological behavior, mechanical properties and water resistance.

2 Materials and Methods

2.1 Materials

Cornstarch (8% moisture) was obtained from Langfang Starch Company (Langfang, Heibei, China). Glycerol and citric acid were purchased from Tianjin Chemical Reagent Factory (Tianjin, China).

2.2 Plasticization

The water content of cornstarch was adjusted to 10 wt% (wet base) by addition of a small quantity of distilled water. Glycerol and water were first mixed, then blended

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(3000 rpm, 2 min) with cornstarch by use of High Speed Mixer GH-100Y (made in China). The mixture was sealed and stored overnight. When citric acid was used, citric acid was firstly dissolved in the additional water. The ratio of glycerol to hydrous corn starch (w/w) was 30:100. The abbreviations for the different samples prepared and their compositions are listed in Tab. 1. Glycerol-plasticized TPS (GPTPS) and citric acid-modified GPTPS (CATPS) were prepared as following: The mixtures were manually fed in to a 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°C, 140°C, 150°C, 130°C (from feed zone to die). The die was a round sheet with 3 mm-diameter holes.

Tab. 1. Used symbols and corresponding sample compositions.

Symbols	Samples [weight proportion]		
	Hydrous starch [wt 10% water content]	Glycerol	Citric acid
GPTPS	100	30	0
CATPS	100	30	>0
CA0.6TPS	100	30	0.6
CA1TPS	100	30	1
CA2TPS	100	30	2
CA3TPS	100	30	3

Noticeably, it was hardly possible for citric acid to react with starch in the extruder, because the cornstarch used contained 10% water, which would restrain esterification of citric acid and starch.

2.3 Scanning electron microscopy (SEM)

The fracture surfaces of extruded TPS strips were analyzed with the scanning electron microscope Philips XL-3 (Eindhoven, The Netherlands), operating at an acceleration voltage of 20 kV. TPS strip samples were frozen in liquid nitrogen, and then broken. The fracture surfaces were vacuum coated with gold for SEM.

2.4 Thermogravimetric analysis (TGA)

The thermal properties of the blends were measured with a ZTY-ZP type thermal analyzer (Beijing University Instrument Factory, Beijing, China). The sample weight varied from 10 to 15 mg. Samples were heated from room temperature to 500°C at a heating rate of 15°C/min.

2.5 Fourier transform infrared (FT-IR) spectroscopy

FTIR spectra were obtained at 2 cm^{-1} resolution with a BioRad FTS3000 IR Spectrum Scanner (Hercules, CA). Typically, 64 scans were signal-averaged to reduce spectral noise. The extruded TPS strips were pressed to transparent slices with a thickness of around 0.2 mm in the Flat Sulfuration Machine (BL 230 * 350, Beijing Plastic Machine Factory, Beijing, China), tested by the transmission method [14].

2.6 X-ray diffractometry

The extruded TPS strips were pressed at 10 MPa with the Flat Sulfuration Machine. The slices were placed in a sample holder for X-ray diffractometry, while the powders were packed tightly in the sample holder. X-ray diffraction patterns were recorded in the reflection mode in the angular range 10–30° (2 Θ) and a scanning rate of 4°C/min at ambient temperature using a BDX3300 diffractometer (Beijing University Instrument Factory, Beijing, China), operated at the CuK$_a$ wavelength of 154.20 nm. The radiation from the anode, operating at 36 kV and 20 mA was monochromized with a 15 μm nickel foil. The diffractometer was equipped with a 1° divergence slit, a 16 mm beam raster, a 0.2 mm receiving slit and a 1° scatter slit. Radiation was detected with a proportional detector.

2.7 Rheology

TPS was cut into small pieces and were tested in a XLY capillary rheometer (Jilin University Instrument Factory, Jilin, China) at temperatures of 130°C, 140°C and 150°C, similar to processing temperature. The radius of the capillary was 1 mm and *L/D* was 40. The test pieces were placed into the barrel of the viscometer through a funnel and then compacted with the plunger until the first extrudate appeared at the capillary exit. The sample was allowed to come to temperature (10–15 min), and was then forced through the capillary by the plunger at preselected velocities. The load on the plunger and plunger speed provide the total pressure drop through the barrel and capillary and the volume flow rate. Shear rate (γ) and shear stress (τ) were calculated by standard methods. In order to understand the TPS processing properties, the rheology experiments were carried out at 130°C, 140°C and 150°C, which covered the processing temperature range.

The melting volumetric flow rate through the capillary is given as

$$Q = \frac{\pi R^3}{4}\gamma\frac{4n}{3n+1} \tag{1}$$

where R = capillary radius, γ = shear rate at the capillary wall, n = flow index depending on the temperature. The term $\frac{4n}{3n+1}$ is the Rabinowitsch correction factor.

Pressures were monitored, and shear stress values were calculated using the following equation:

$$\tau = \frac{\Delta P \cdot R}{2L} \tag{2}$$

where ΔP = pressure at the capillary entrance, L = capillary length, R = capillary radius.

According to *Onteniente* et al. [15], thermoplastic starch exhibits power-law behavior:

$$\tau = K\gamma^n \tag{3}$$

The apparent viscosity η is defined by Equation (4):

$$\eta = \tau / \gamma \tag{4}$$

where τ = shear stress, γ = shear rate at the capillary wall, K = consistency index of the materials depending on the temperature, the structure and the formulation of the polymer.

Substituting Equation (4) for τ in the relationship (3) between τ and γ yields:

$$\eta = K\gamma^{n-1} \tag{5}$$

$$\lg\eta = \lg K - (1-n)\lg\gamma \tag{6}$$

If $y = \lg\eta$ and $x = \lg\gamma$, then the linear fit equation:

$$y = \lg K - (1-n)x \tag{7}$$

According to the Arrhenius equation:

$$\eta = A \cdot e^{\Delta E_\eta / RT} \tag{8}$$

$$\lg \eta = \lg A + \Delta E_\eta / (RT \cdot \ln 10) \tag{9}$$

where ΔE_η is the activation energy of viscous flow, A the consistency related to structure and formulation, and R the gas constant ($8.314 \, \mathrm{Jmol^{-1}K^{-1}}$).

2.8 Mechanical testing

Samples of 80 mm × 3 mm in size were cut from the extruded strips and pressed with the Flat Sulfuration Machine. The Testometric AX M350–10KN Materials Testing Machine was operated at a crosshead speed of 10 mm/min for tensile testing (ISO 1184–1983 standard). The data given are averages of the results of 5–8 specimens.

2.9 Storage conditions and water contents

In order to analyze the effect of environmental humidity on TPS retrogradation and water absorption, the strips for mechanical testing were stored in closed containers over several materials at 20°C for a period of time. These materials were dried silica gel, substantive 35.64% $CaCl_2$ solution, NaCl saturated solution and distilled water, providing relative humidity (RH) 0, 50, 75 and 100% environments, respectively. The slices for X-ray diffractometry were stored at RH 0, 50 and 100%.

Water contents were determined gravimetrically by drying small pieces of TPS at 105°C overnight in an oven. At this condition, evaporation of glycerol and formamide was negligible [16].

3 Results and Discussion

3.1 SEM analysis

The morphology of native cornstarch granules, of GPTPS and CA1TPS at 500 × magnification is shown in Fig. 1. In the continuous phases of CA1TPS and GPTPS no residual granular structures are left and the fracture face of CA1TPS is smoother than that of GPTPS. The acidity of citric acid promotes the fragmentation and dissolution of cornstarch granules. Glycerol and citric acid were known to disrupt intermolecular and intramolecular hydrogen bonds and plastify native starch at the high shear and temperature conditions.

3.2 Thermogravimetric analysis

Fig. 2 presents TGA curves of GPTPS, CA1TPS and CA3TPS. The mass loss below 100°C was mainly ascribed to water loss. However, citric acid decreased water loss in CATPS, compared to GPTPS. The mass loss from 100°C to the onset temperature of thermal decomposition was related to the evaporation of both water and plasticizers, so the difference in the decomposition onset and mass loss at onset temperature was mainly due to the volatility of glycerol and water in TPS with different citric acid contents. CATPS had higher onset temperature and lower mass loss than GPTPS. This indicated that the presence of citric acid increased the binding of both water and glycerol to starch. As shown in Fig. 2, the temperature of starch thermal decomposition varied from 300°C to 330°C with the increase in citric acid contents. Citric acid increased the temperature of thermal decomposition of starch, because citric acid can form stronger hydrogen-bonds with starch than glycerol. Therefore, the improvement in thermal stability confirms that, with the addition of citric acid, the adhesion between citric acid, glycerol, water and starch in TPS is enhanced.
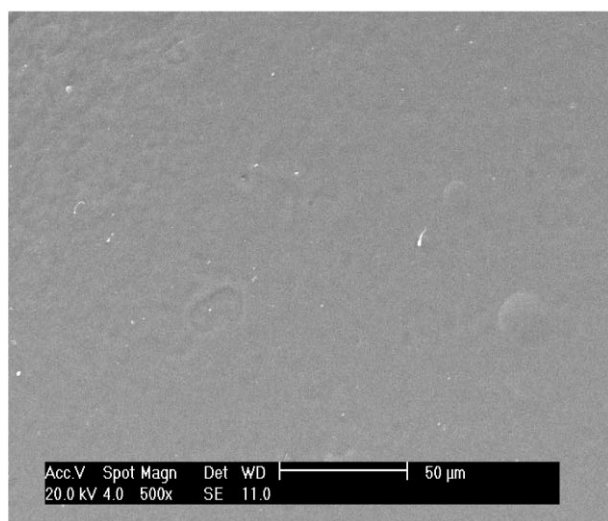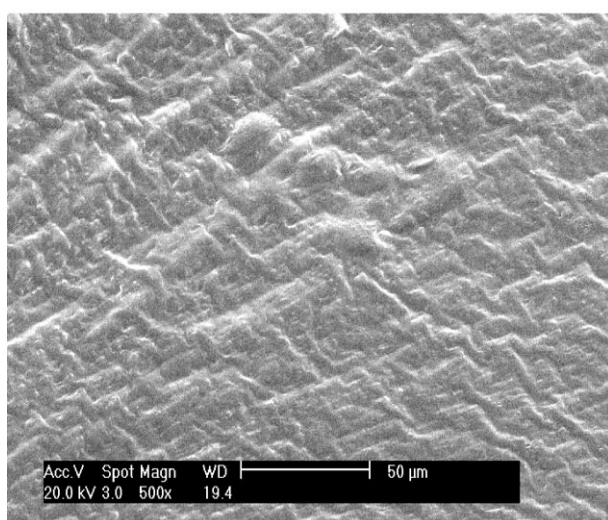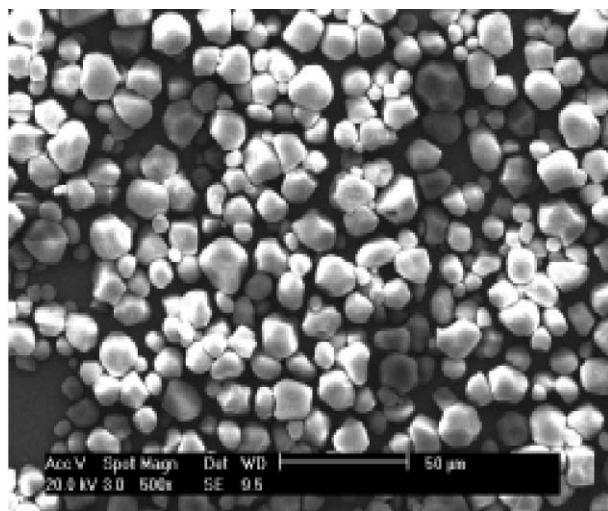
Fig. 1. SEM micrograph of native corn starch granules (top), GPTPS (middle) and CA1TPS (bottom) at 500 × magnification.

As a side reaction possibly acidolysis of starch occurred, however not to a large extent. Otherwise citric acid would obviously decrease the thermal stability of TPS.

3.3 Retrogradation

3.3.1 FTIR

The changes in FTIR spectra with storage time can be used to monitor starch retrogradation [17–19]. FTIR spectra for GPTPS (top) and CA1TPS (bottom), stored for 0 day and 70 days are shown in Fig. 3. The FTIR analysis was based on the identification of absorption bands resulting from the vibrations of functional groups in starch and plasticizers. The wave numbers related to vibrations of the C-O groups of starch are shown in Tab. 2. Compared to native starch, the three characteristic peaks of starch in the FTIR spectra of all TPS are shifted to lower wave number. Both C-O-H and C-O-C groups in starch can form hydrogen bonds with glycerol, which decreases the stretching vibration wave numbers of the C-O group of C-O-C in starch at 1020 cm^{-1} and of the C-O group of C-O-H in starch at 1156 cm^{-1} and 1081 cm^{-1}. Compared to GPTPS (0 day storage time), the vibration of the C-O group of C-O-C in CA1TPS (0 day storage time) was shifted to a lower wave number. This reveals that hydroxyl and carboxyl groups of citric acid form stronger interactions with C-O groups of C-O-C in starch than glycerol.

Tab. 2. Influence of storage time on the vibration wave number of C-O groups of starch in FT-IR spectrum.

TPS (storage time)	Vibration wave number [cm^{-1}]			
	C-O of C-O-H in starch		C-O of C-O-C in starch	
Native starch	1156	1081		1020
GPTPS (0 day)	1150	1078	1014	–
GPTPS (70 days)	1150	1078	1016	996
CA1TPS (0 day)	1150	1078	1012	990
CA1TPS (70 days)	1150	1078	1012	990

As shown in Fig. 3 (top) and Tab. 2, a change in the FTIR spectrum was accompanied by the formation of thermoplastic GPTPS (0 day storage time) and its retrogradation (70 days storage time). At 0 day storage time the GPTPS showed a broad absorption peak at 1014 cm^{-1}. After 70 days, this broad peak was separated into two peaks at 1016 cm^{-1} and 996 cm^{-1}. This can be explained by a reduction of hydrogen-bond interactions between starch and glycerol in GPTPS during the storage, which is essential to starch re-crystallization in GPTPS.
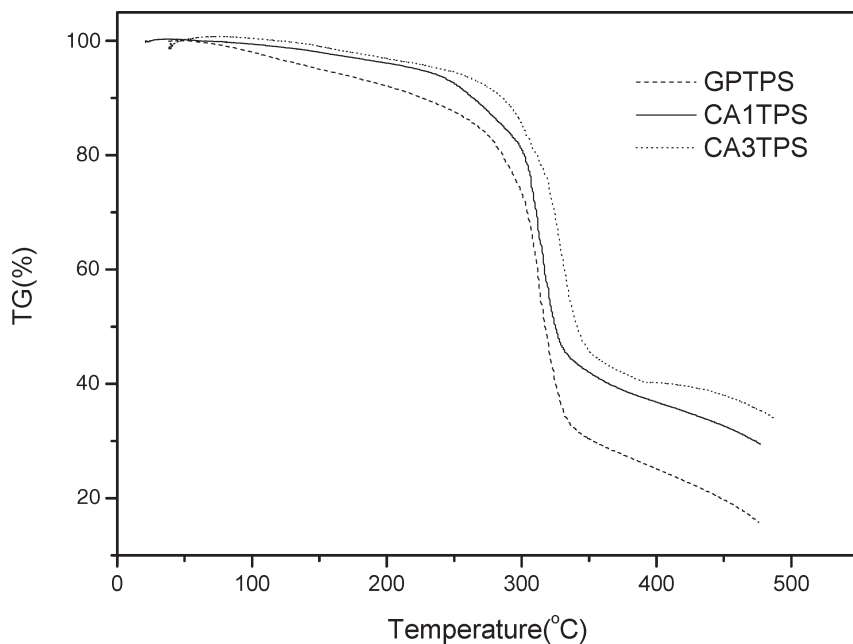
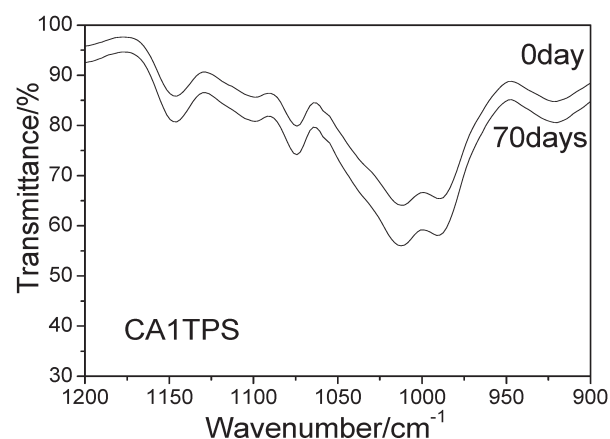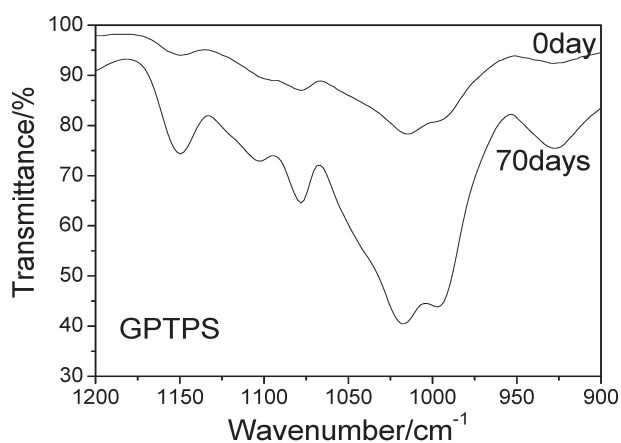**Fig. 2.** Effects of citric acid on TGA of TPS.

Fig. 3. FTIR spectra for GPTPS (top) and CA1TPS (bottom) stored for 0 day and 70 days.

The effect of citric acid on the retrogradation of CA1TPS was also studied. Fig. 3 (bottom) shows that no significant change in the FTIR pattern of the C-O group is observed with increasing storage time. This demonstrates that citric acid can protect the CA1TPS from retrogradation. Citric acid interacts more strongly with the C-O group than glycerol, and consequently prevents the formation of hydrogen bonds between the hydroxyl groups of TPS in the amorphous state. This prevention of hydrogen-bond formation results in a low degree of re-crystallization, i.e. retrogradation.

3.3.2 X-ray diffractometry

Fig. 4 shows the X-ray diffraction patterns of GPTPS and CATPS with different citric acid contents stored at relative humidity (RH) of 0, 50% and 100% for 0 and 70 days. Compared to native cornstarch (shown in Fig. 4a), the crystal structure of TPS is largely changed. During processing, glycerol and citric acid molecules enter into the starch particles, then replace starch intermolecular and intramolecular hydrogen bonds and destroy the crystallinity of starch. Therefore, the A-type crystallinity of native cornstarch [20] is lost and no crystals can be detected in both GPTPS and CATPS.

As shown in Fig. 4 b–d, the effect of water on starch retrogradation is significantly different between GPTPS and CATPS. After TPS were separately stored at RH 0, 50% and 100% for 70 days, CATPS was still amorphous, however crystallinity was found for GPTPS. GPTPS
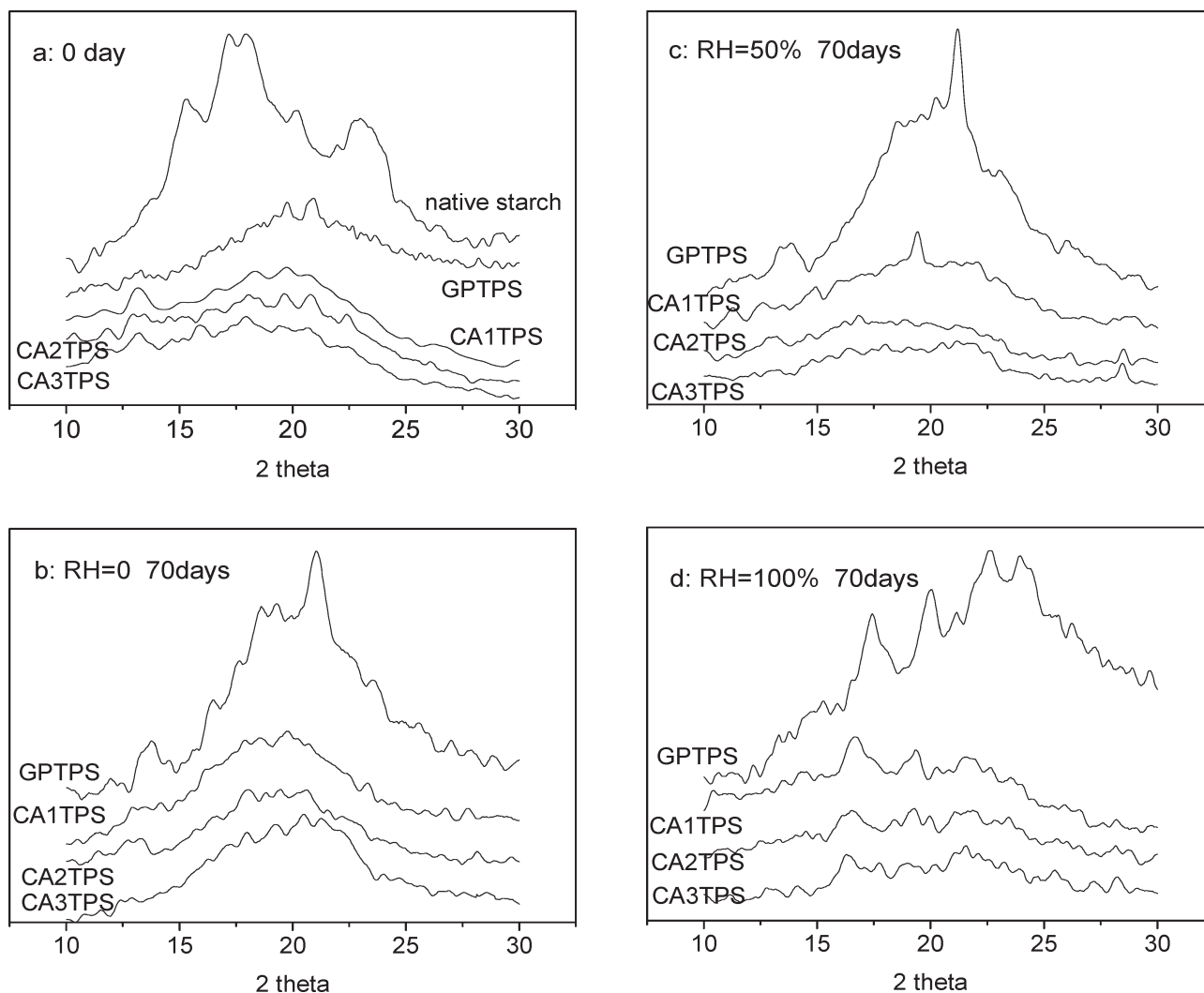
Fig. 4. X-ray diffraction patterns of GPTPS and CATPS stored at RH 0, 50% and 100% for 0 and 70 days.

stored at RH 0 and 50% for 70 days showed V_a-type crystallinity, i.e. double-helix conformation [20, 21], while GPTPS stored at RH 100% for 70 days showed a B-type structure, i.e. single-helix conformation [20, 21]. In GPTPS, the additional water favored starch re-crystallization. However water had little effect on starch retrogradation in CATPS.

The retrogradation of TPS is greatly dependent on the hydrogen bond-forming abilities of plasticizers with starch molecules. The stronger the hydrogen bond between starch and the plasticizer, the more difficult it is for starch to re-crystallize during the storage time of TPS. Citric acid is advantageous for suppressing starch retrogradation, because citric acid can form stronger hydrogen-bond interactions with starch than glycerol, as prov-

en by FTIR (in Fig. 3). A small quantity of citric acid (e.g. 1 wt%) is enough to inhibit starch retrogradation, even at high relative humidity.
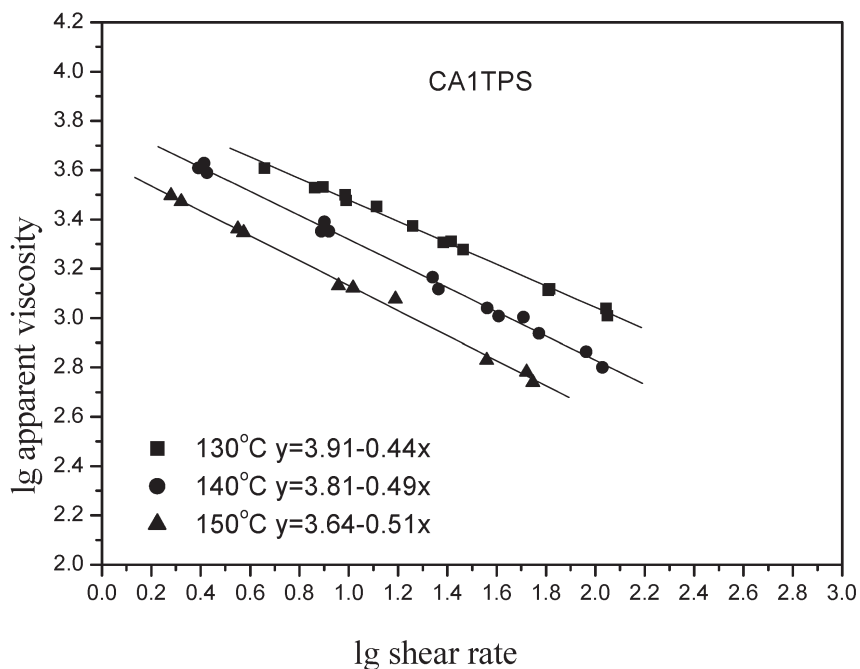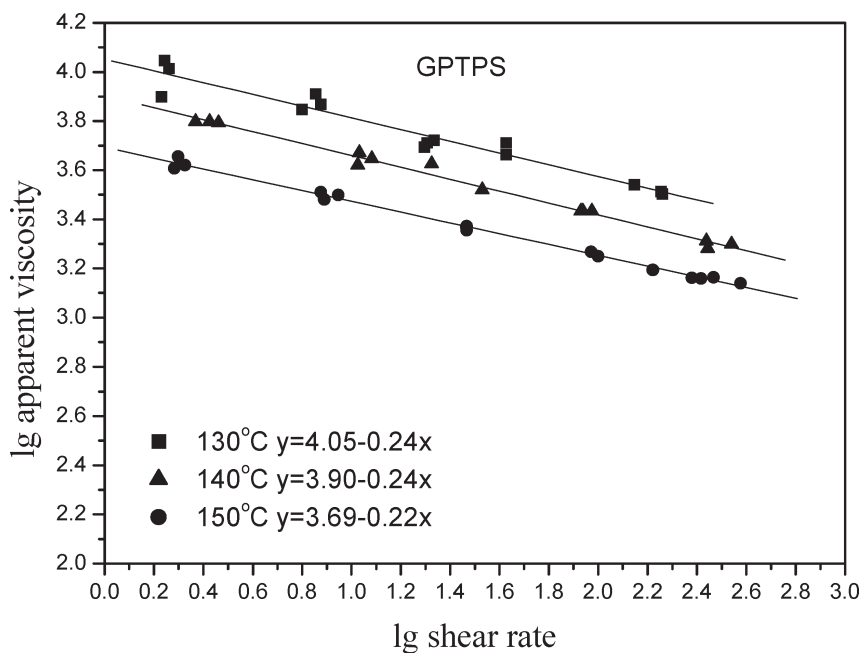
3.4 Rheology

Double logarithmic plots of the $\eta \sim \gamma$ curves are shown in Fig. 5. Both TPS show shear-thinning behavior, which is mainly ascribed to the gradual reduction of starch intermolecular bonds.

As shown in Fig. 5, both citric acid content and temperature largely influence the TPS rheological behavior. According to the listed linear fit equations in Fig. 5, the apparent viscosity η of TPS decreases with increasing temperature and with increase in citric acid content at the same temperature.

The flow index n, K and viscous flow activation energy ΔE_η of TPS at 130°C, 140°C and 150°C are listed in Tab. 3. According to Equation (7), linear fit equations are listed in both Fig. 5 and Tab. 3. The slope of the linear fit equation is $-(1-n)$ and the intercept lg K.

The flow index n decreases with the increase in citric acid content, which means that the introduction of citric acid makes TPS more sensitive to the shear rate. On the other hand, K also decreases with the increasing of citric acid content and the temperature. This is because citric acid can form strong bonding interactions with starch and weaken the interaction of starch molecules, facilitating the slippage movement among starch molecules. Another reason for this behavior can be the acidolysis of starch in the presence of citric acid.
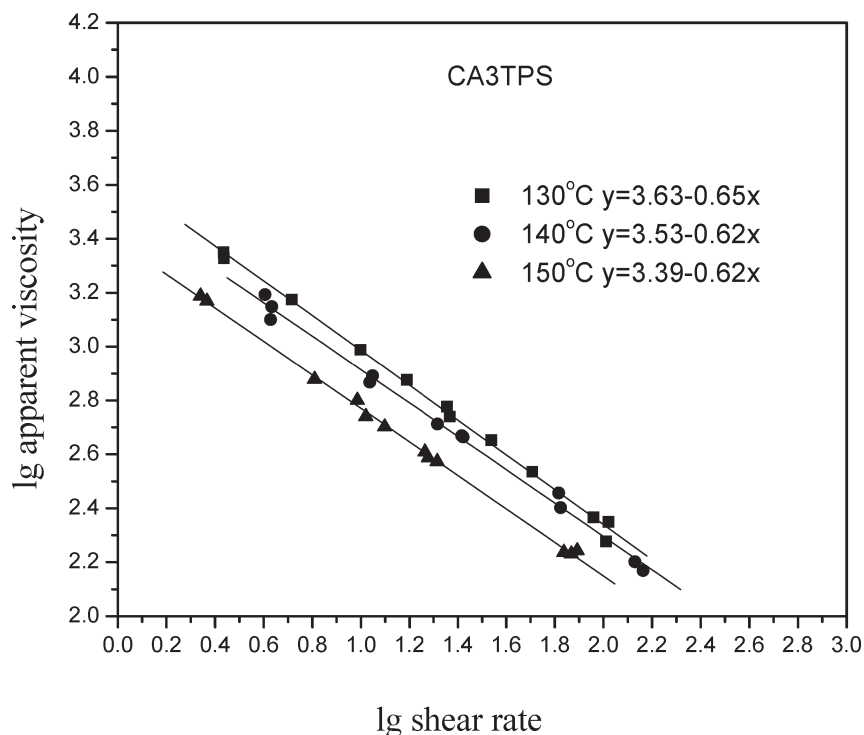
Fig. 5. Rheology curves of GPTPS and CATPS at 130°C, 140°C and 150°C.

Tab. 3. Effect of citric acid contents on the viscous flow activation energy ΔE_η (x=0) and flow index *n* of TPS at 130°C, 140°C and 150°C

Samples		GPTPS	CA1TPS	CA3TPS
130°C	Linear Eq.	y= 4.05–0.24x	y=3.91–0.44x	y=3.63–0.65x
	n	0.76	0.56	0.35
	K	11220	8128	4266
140°C	Linear Eq.	y=3.90–0.24x	y=3.81–0.49x	y=3.53–0.62x
	n	0.76	0.51	0.38
	K	7943	6457	3388
150°C	Linear Eq.	y=3.69–0.22x	y=3.64–0.51x	y=3.39–0.62x
	n	0.78	0.49	0.38
	K	4898	4365	2455
ΔE_η (x=0)	(kJ/mol)	50.86	43.95	39.08

Citric acid can obviously decrease the shear viscosity and improve the fluidity of TPS, which would be advantageous for blending of TPS and biodegradable resins. In fact, citric acid widens the processing temperature range of GPTPS, thus minimizing melt temperature differences between TPS and biodegradable resins during coextrusion [6].

According to Equation (9), lg η (x=0) ~1/*T* curves were linearized to calculate ΔE_η from the slope (ΔE_η /(RIn10)). The viscous flow activation energy ΔE_η represents the effect of the temperature on the behavior of TPS. The higher ΔE_η, the more temperature-sensitive the behavior of TPS is. According to the values of ΔE_η (x = 0) in Tab. 3, CATPS is less sensitive to processing temperature when the citric acid contents increases.

Therefore, during the thermoplastic processing the extruder screw speed can effectively adjust the flow behavior of CATPS, while the processing temperature can effectively adjust the flow behavior of GPTPS.

3.5 Mechanical properties

Fig. 6 showed the effect of citric acid contents on the mechanical properties of TPS, which were immediately bagged after thermoplastic processing and stored for one week at RH 50% in the plastic bags before testing.

Compared to GPTPS (elongation 85%), the elongation of CATPS was increased. Citric acid can form strong interactions with starch and weaken the interaction of starch molecules, thus facilitating the slippage among starch molecules. The elongation of CA0.6TPS, CA1TPS, CA2TPS and CA3TPS, respectively, reached 150%, 125%, 138% and 100%. However, the change in elongation was not proportional to the increase in citric acid content. The introduction of citric acid decreased the tensile stress. The higher the citric acid content was, the more the tensile stress decreased. The tensile stress of CA3TPS was only 1.45 MPa.

3.6 Water absorption

Water sensitivity is another important criterion for many practical applications of TPS. Fig. 7 shows the dependence of water contents in TPS with different citric acid contents on storage time at RH 75% and 100%. The equilibrium water content of GPTPS was about 38% and 47% at RH 75% and 100%, respectively, while the equilibrium water content of CATPS varied with citric acid contents from 23.6% to 26% at RH 75% and from 36% to 38% at RH 100%. The addition of citric acid improved the water resistance of TPS at high relative humidities, however, the equilibrium water content of CATPS varied little when citric acid contents increased from 0.6% to 3%.

4 Conclusions

Citric acid can form stable hydrogen-bond interactions with starch, which effectively prevented starch retrogradation when CATPS were stored at RH 0, 50% and 100% for 70 days. Citric acid can obviously decrease the shear viscosity and improve the fluidity of TPS. Therefore, citric acid widens the processing temperature scopes of GPTPS, which would avoid melt temperature differences between TPS and biodegradable resins during coextrusion. The introduction of citric acid improves the thermal stability, the elongation of GPTPS, but decreases the tensile stress. Citric acid can improve water resistance of GPTPS at high relative humidities.
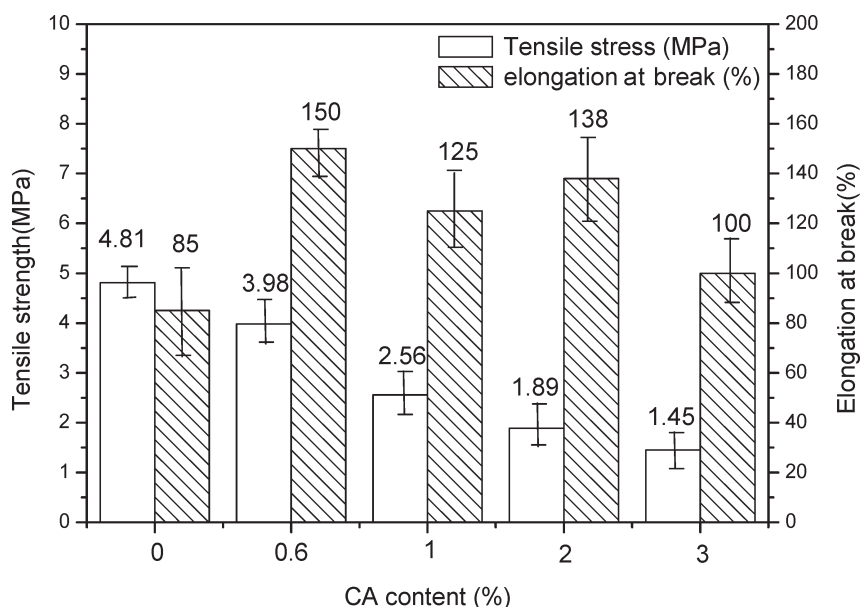

Fig. 6. Effect of citric acid contents on mechanical properties of TPS.
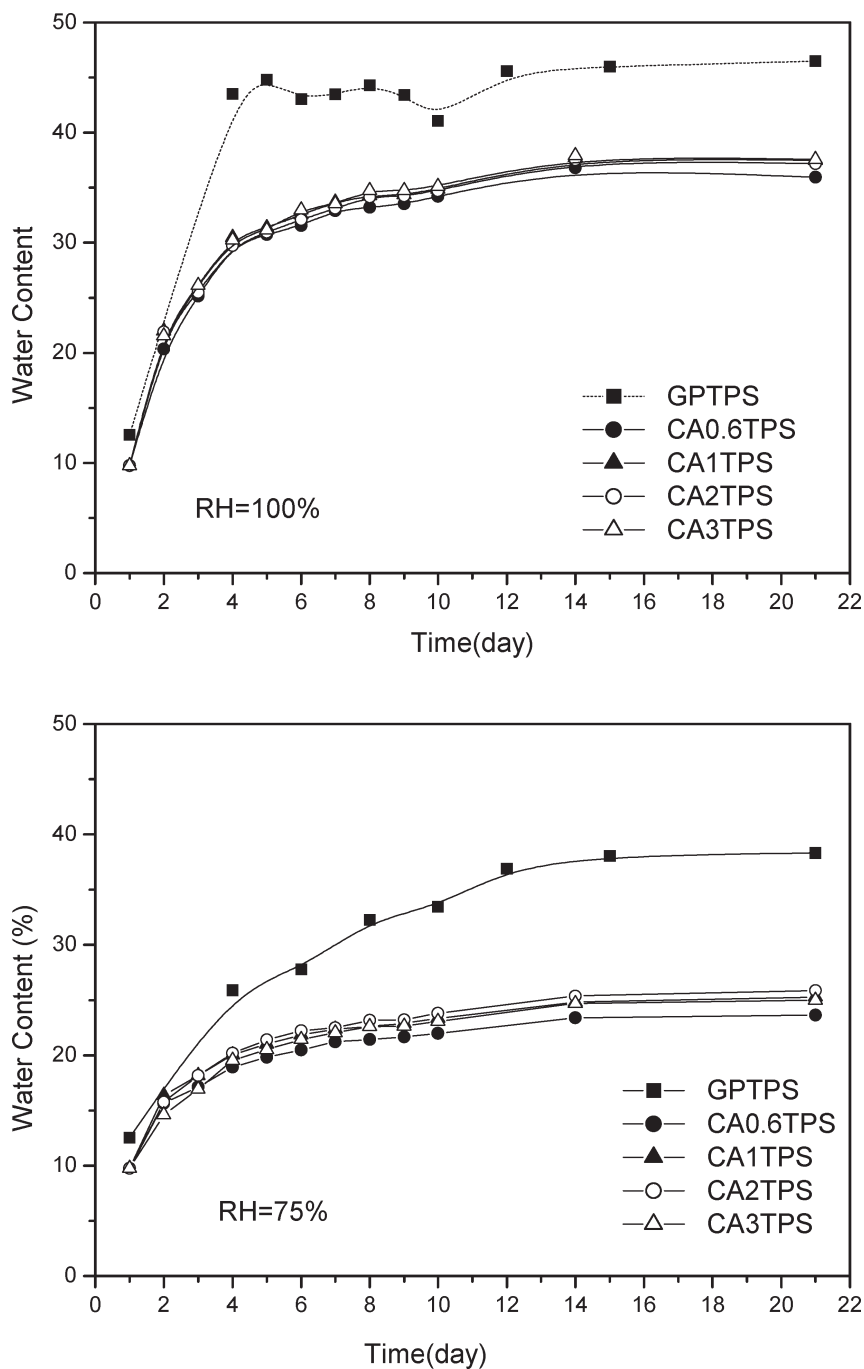
Fig. 7. Dependence of water contents in TPS on different citric acid contents and storage time at RH 75% and 100%.

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