Available online at www.sciencedirect.com
ScienceDirect
Carbohydrate Polymers 67 (2007) 446–453
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

The influence of citric acid on the properties of thermoplastic starch/linear low-density polyethylene blends

Wang Ning, Yu Jiugao *, Ma Xiaofei, Wu Ying

School of Science, Tianjin University, Tianjin 300072, China

Received 7 December 2005; received in revised form 19 May 2006; accepted 10 June 2006
Available online 25 September 2006

Abstract

The effects of citric acid (CA) on the properties of glycerol/starch/linear low-density polyethylene (LLDPE) blends were studied. The plasticization of starch and its blending with PE were accomplished in one-step processing. The presence of CA improved the dispersion and the plasticization of starch, shown by scanning electron microscope (SEM). At the same time, the mechanical properties of the blends dramatic increased. The rheological study proved that acidic CA could decrease the shear viscosity and improve the fluidity of TPS/PE blends. Fourier transform infrared (FT-IR) spectroscopy proved that CA could weaken the interaction of starch molecules and improve the plasticization of starch. The X-ray diffractometry showed that starch was plasticized more completely in the CATPS/PE blends. CA could also ameliorate the water resistance of TPS/PE blends at different relative humidities.

Keywords: Thermoplastic starch; Citric acid; Linear low-density polyethylene

1. Introduction

Today polyethylene (PE) is widely used as packaging material and mulch film in agricultural application. After their usage these discarded polymers are a significant source of environmental pollution, harming wildlife. In order to accelerate the biodegradation and depress the cost, starch as an inexpensive, renewable and natural polymer has been used to blend with PE (Willett, 1994). Because of the strong intermolecular and intermolecular hydrogen bonds in starch, native starch cannot be processed as a thermoplastic material. But in the presence of plasticizers, for example, glycerol (Fishman, Coffin, Konstance, & Onwulata, 2000; Forssell, Mikkilä, Moates, & Parker, 1998; Liu, Yi, & Feng, 2001), glycol (Yu, Gao, & Lin, 1996), sorbitol (Wang, Shogren, & Carriere, 2000), formamide and urea (Ma & Yu, 2004), etc., accompanying with high temperatures and under shear, a deformable thermoplastic material can be achieved. These plasticized starches are commonly called thermoplastic starches (TPS) (Stepto, 2003). It can increase the properties of the blends and the content of TPS in TPS/PE blends (Rodriguez-Gonzalez, Ramsay, & Favis, 2003).

TPS can be processed with traditional processing conditions (extrusion, blow molding and injection molding). In order to increase the fluidity of molten TPS, Carvalho, Zambon, Curvelo, and Gandini (2005) use carboxylic acids to decrease the viscosity of TPS through controlling the macromolecules of starch. After melt processing in the presence of glycerol, water and carboxylic acids, both the molar masses and viscosity of TPS are decreased. In our previous work (Yu, Wang, & Ma, 2005) citric acid (CA) is also used as additive to modify TPS during melt processing. CA can effectively restrain starch re-crystallization, except for increasing the fluidity of TPS. But the mechanical properties of TPS are decreased, especially the tensile strength (below 4 MPa).

---

* Corresponding author. Tel.: +86 022 27401644; fax: +86 022 27403475.
E-mail address: wnares@eyou.com (Y. Jiugao).

0144-8617/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2006.06.014

So in the presence of CA, “one-step extrusion” is adapted to process glycerol/starch/LLDPE blends with single-screw extruder in this paper. Compared with the glycerol/starch/LLDPE blends, CA can dramatic increase the mechanical properties of the blends. At the same time, the fractured surface micrograph, rheology, the hydrogen bonds in the blends, crystal capability and water resistance are also studied in this paper.

2. Experimental

2.1. Materials

The linear low-density polyethylene (LLDPE 7042) was purchased from Jilin Petrochemical Filiale (Jilin, China). The native cornstarch (ST, 12% moisture), containing 30 wt% amylose and 70 wt% amylopectin, was obtained from Langfang Starch Co. (Langfang, Hebei, China). The plasticizer, glycerol, was purchased from Tianjin Chemical Reagent Factory (Tianjin, China). Citric acid (CA) was purchased from Tianjin Chemical Reagent Factory.

2.2. Samples preparation

Blending was carried out by use of a high-speed mixer GH-100Y (made in China) at room temperature. The rotor rate was maintained at 3000 rpm for 2 min, adding LLDPE and starch first, then adding glycerol and CA. The symbol and relevant sample components were listed in Table 1. The mixtures were manually fed into a laboratory-scale SSE SJ-25(s) (screw diameter (d) = 30 mm, screw ratio L/D = 25:1, made in China). The extrusion conditions were as follows: the temperature profile along the extruder barrel: 145–150–145–130 °C (from feed zone to die). The screw speed was 10 rpm. The die was a round sheet with 3-mm-diameter holes.

2.3. Mechanical properties of blends

Measurements of the mechanical properties, such as tensile strength and elongation at break, were performed according to the method detailed in ASTM D828-88 (ASTM 1989) on a Testometric AX M350-10KN Materials Testing Machines. Measurements were done using a 100 mm min^{-1} crosshead speed. Before the measurement, the samples were conditioned at 50% relative humidity for 48 h at an ambient temperature in a closed chamber containing a 33.46 wt% $CaCl_2$ solution in a beaker. Ten measurements were conducted for each sample and the results were averaged to obtain a mean value.

Table 1
The symbols and relevant sample components

Symbols	Samples (weight proportion)			
	Starch	Glycerol	LLDPE	Citric acid
GPTPS	70	30	0	0
CA2TPS	70	30	0	2
GPTPS/PE	70	30	100	0
CA0.6TPS/PE	70	30	100	0.6
CA1TPS/PE	70	30	100	1
CA2TPS/PE	70	30	100	2
CA3TPS/PE	70	30	100	3

2.4. Scanning electron microscopy (SEM)

The fracture surfaces of extruded TPS/PE blend strips were performed with Scanning Electron Microscope Philips XL-3, operated at an acceleration voltage of 20 kV. TPS/PE strip samples were cooled in liquid nitrogen, and then broken. The fracture surfaces were vacuum coated with gold for SEM.

2.5. Rheology

The capillary viscometer used to determine the viscosity of the blends was XYL-II capillary rheometer. The capillary viscometer consists of a barrel into which material was loaded before being pushed by a plunger through a capillary was controlled by a surrounding heating unit. The radius of capillary was 1 mm and L/D was 40. The small pieces were placed into the barrel through a funnel and then packed down 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 pre-selected velocities. The load on the plunger and plunger speed provide the total pressure drop through the barrel and capillary and the volume flow rate.

2.6. Fourier transform infrared (FT-IR) spectroscopy

The IR spectra were measured with BIO-RAD FTS3000 IR Spectra Scanner. The extruded TPS strips were pressured to the transparent slices with the thickness of around 0.2 mm in the Flat Sulfuration Machine, tested by the transmission method (Pawlak & Mucha, 2003).

2.7. X-ray diffractometry

The extruded blends strips were pressured 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 angular range 10–30° (2θ) at the ambient temperature by a BDX3300 diffractometer, operated at the Cu K_α wavelength of 1.542 Å. The radiation from the anode, operating at 36 kV and 20 mA, monochromatized with a 15 μm nickel foil. The diffractometer was equipped with 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.

2.8. Water absorption property

The bars of sample were cut into small pieces, and weighed immediately, then put into the oven, dried at 105 °C for 24 h. These small pieces of sample were weighed immediately after being taken out. The water content rate (*K*) took the following formulation:

$$K = \frac{w_2 - w_1}{w_1} 100\%,$$

in which, w_2 is the mass of the wet sample and w_1 is the mass of the dried sample.

The samples were stored at different relative humidity conditions for a period of time, then taken out and weighed immediately. The water content rates (*K*) at different relative humidity were calculated.

3. Results and discussion

3.1. Blends morphology

It was well known that PE and TPS could form immiscible blends because of the high interfacial tension between a non-polar polymer and a highly polar one. So it was very necessary to study the morphology structure of immiscible polymer blends to understand many properties (Willemse, de Posthuma, van Dam, & Gotsis, 1998), especially the mechanical properties. It could be seen from SEM of GPTPS/PE blends (Fig. 1(A)), the sample surface was uneven. The residual starch granules were obviously not disrupted and some of them were removed from the sample surface and left some cavities in the fracture surface. It could be certain that no polar PE deteriorated the plasticization of starch in one-step extrusion. At the same time, GPTPS/PE blends displayed a discrete morphology and the interface between TPS and PE was very clear, which were indicated with white arrow in Fig. 1(A). It was ascribed to the high interfacial tension between a non-polar polymer and a highly polar one.

Compared to GPTPS/PE blends, the microscopic morphology of CATPS/PE blends was shown in Figs. 1(B) and (C). With increasing the content of CA in CATPS/PE blends, the dispersion between TPS and PE was improved and TPS particles volume markedly decreased. Especially, in Fig. 1(C) CA2TPS/PE blends turned into an evenly continuous phase system. In addition, the fracture surface of the blends became more and more smooth. It was well known that the acidity of CA was propitious to fragmentation and dissolution of cornstarch granules, which improved the plasticization of starch at the high shear and temperature conditions (Carvalho et al., 2005; Forssell et al., 1998; Ma & Yu, 2004; Yu et al., 2005). So with improving the fluidity of TPS, it would be more propitious to blending TPS with PE.

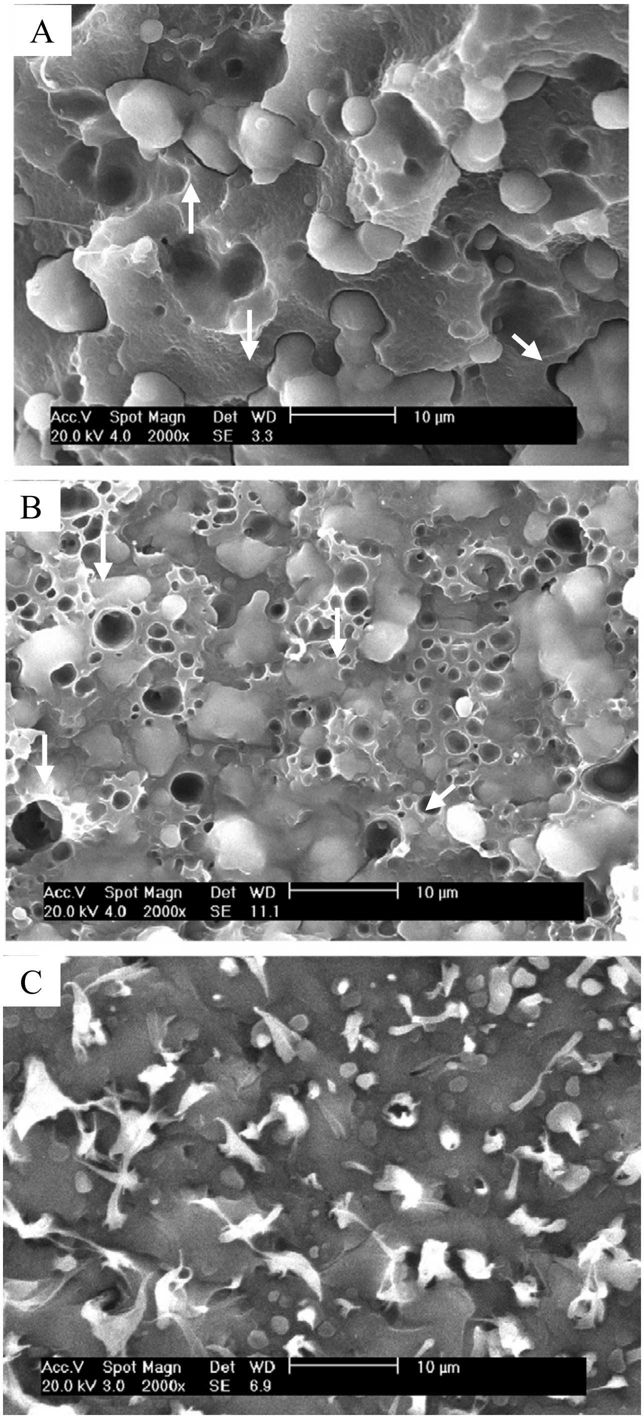

Fig. 1. The SEM photographs of the TPS/PE blends. (A) GPTPS/PE 2000×; (B) CA0.6TPS/PE 2000×; (C) CA2TPS/PE 2000×.

3.2. Mechanical properties

As shown in Fig. 2, the mechanical properties of TPS/PE blends without CA were very poor, especially the tensile strength, which ascribed to unthermoplastic starch granules and the poor interfacial adhesion between two different polarity materials (can be seen from Fig. 1(A)). But the tensile strength and the elongation at break of the blends were greatly enhanced in the presence of CA. The

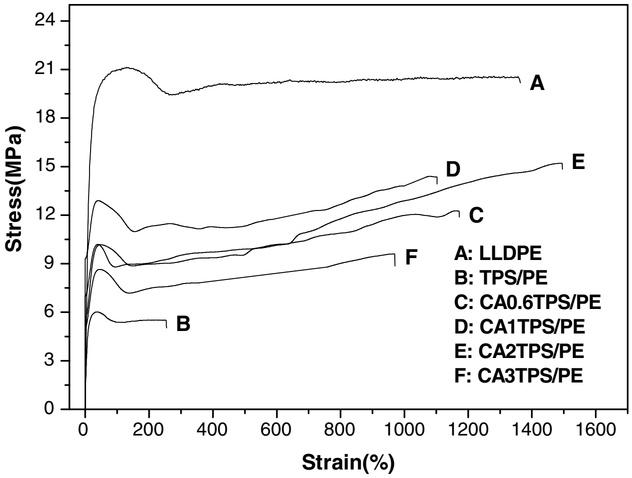

Fig. 2. The mechanical properties of LLDPE and TPS/PE blends.

maximum tensile strength and the elongation at break of CATPS/PE blends were, respectively, 15.2 MPa and 1493.6% when the content of CA was 2% in the blends, which was similar to pure PE, especially the elongation at break. However, the mechanical properties of the blends decreased when the content of CA was more than 3%. The high content of CA might make starch badly acidolysis, which deteriorated the rigid structure of starch completely.

3.3. Rheology

In order to understand the TPS/PE processing properties, the rheology experiments were carried at 130, 140 and 150 °C, which covered the processing temperature range. Shear rate (γ) and shear stress (τ) were calculated by standard methods, which could be referenced in our previous work (Yu et al., 2005).

The η–γ curves were plotted using a double logarithmic (in Fig. 3). With increasing shear stress the viscosity of each blend decreased. Such flow behavior was called shear thinning, which was mainly ascribed to the increasing orientational degree and the deterioration in chain entanglement of both PE and TPS. In GPTPS/PE, TPS and LLDPE were not well dispersed (shown in SEM micrographs), and the adhesion between TPS and LLDPE was poor. The residual rigid starch particles and the molecular orientation might prevent the molten blend from flowing smoothly at the experimental temperatures, so apparent viscosities were high. In CATPS/PE blends, the arrangement of molecules was more orderly than that of GPTPS/PE because of the good starch plasticization and the high dispersion between TPS and LLDPE.

As shown in Fig. 3, the effect of both CA content and the temperature on rheological behavior of TPS/PE blends was much. According to the listed linear fit equations in Fig. 3, blends were prone to the flow along with the increasing temperature, and the apparent viscosity η was decreasing with the increasing of CA content at the same temperature. These observations indicated the macromolecular fragmentation was not mainly due to either mechanical shearing or high temperature, but the specific action of the added CA.

The flow index n, K and viscous flow activation energy (ΔE_η) of TPS/PE blends at 130, 140 and 150 °C, were listed in Table 2. According to the previous work, (Yu et al., 2005) linear fit equations were listed in both Fig. 3 and Table 2. The slope of linear fit equation was $-(1-n)$ and the intercept was $\lg K$.

The flow index n increased with the increasing of CA contents. It meant that the introduction of CA made TPS/PE blends more sensitive to the shear rate. On the other hand, K also decreased with the increasing of CA content and the temperature. Because acidity of CA was propitious to fragmentation and dissolution of cornstarch granules deteriorated the chain entanglement in starch and weakened the interaction of starch molecules, the slippage movement among starch molecules was facile. So with decreasing the shear viscosity and improving the fluidity of TPS, it would be more propitious to blending between TPS and PE. Generally, TPS hardly dispersed well in runny resin because of poor TPS fluidity.

According to Arrhenius equation:

$$\eta = A \cdot e^{\Delta E_\eta / RT}, \tag{1}$$

$$\lg \eta = \lg A + \Delta E_\eta / (RT \cdot \ln 10), \tag{2}$$

where ΔE_η is the viscous flow activation energy, A is the consistency related to structure and formulation, R is the gas constant 8.314 J mol^{-1} K^{-1}.

$\lg \eta$ $(x=0)$–$1/T$ curves were linearized, and then $\Delta E_\eta/(R \ln 10)$ was the slope. The viscous flow activation energy ΔE_η represented the effect of the temperature on the behavior of blends. The more ΔE_η was the more sensitive the behavior of blends were to the temperature. According to the values of ΔE_η $(x=0)$ in Table 2, CATPS/PE blends were less sensitive to processing temperature with the increasing of CA contents.

Therefore, during the thermoplastic processing the extruder screw speed could effectively adjust the flow behavior of TPS/PE blends, while processing temperature could effectively adjust the flow behavior of the blends.

3.4. Fourier transform infrared (FT-IR) spectroscopy

Figs. 4(A–C) showed FT-IR spectra of GPTPS/PE, CA1TPS/PE and CA3TPS/PE blends. For the compatible polymer blends, FT-IR spectra band would deviate greatly or obviously displace (the band's frequency shifting and the peak style asymmetrically widening) compared with that of the single polymer component. However, for the completely incompatible polymer blends, the characteristic absorption spectra would overlap perfectly compared with the single polymer component (Pei-xi & Liu-cheng, 1996). As shown in Fig. 4, there were several characteristic peaks of starch between 995 and 1156 cm^{-1}, attributed to C–O–C

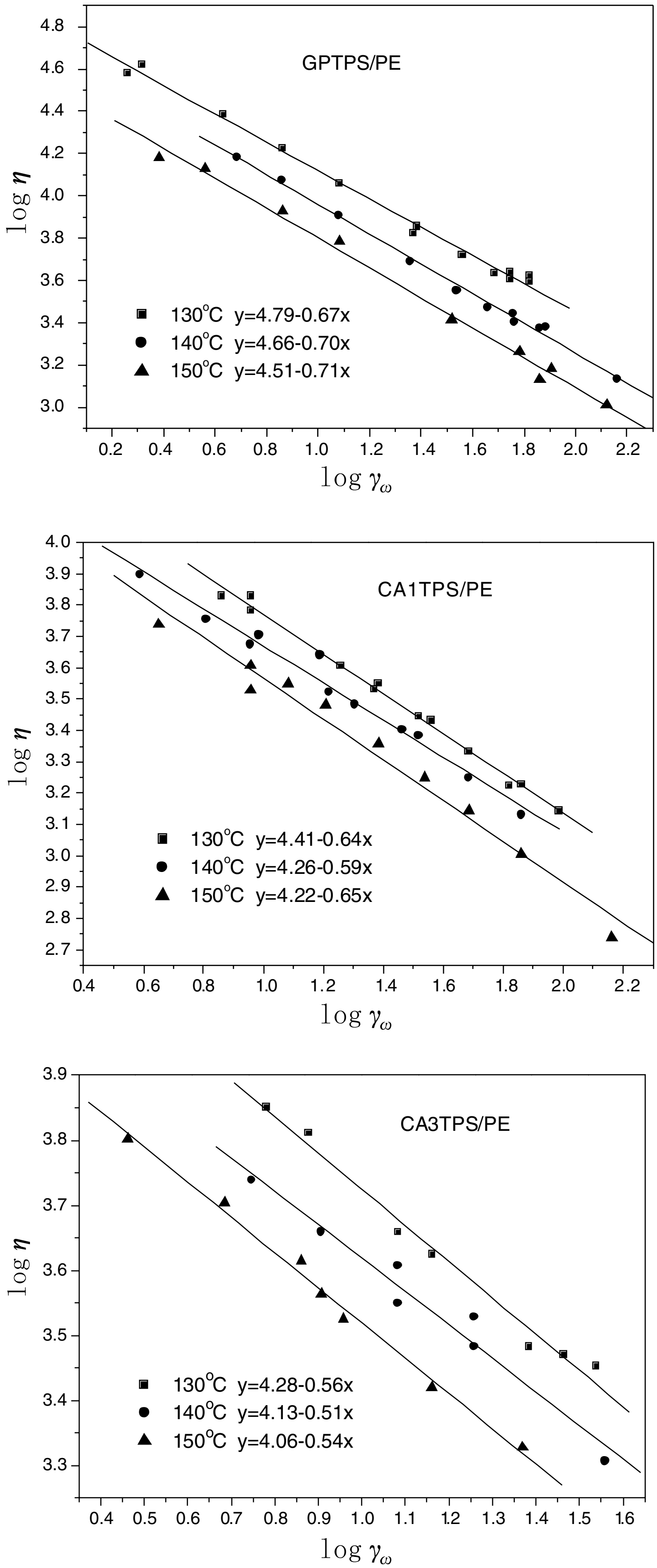

Fig. 3. The rheology curves of GPTPS/PE and CATPS/PE at 130, 140 and 150 °C.

Table 2
The effect of CA contents on the vicious flow activation energy ΔE_η ($x = 0$) and flow index n of TPS/PE blends at 130, 140 and 150 °C

Samples		TPS/PE	CA1TPS/PE	CA3TPS/PE
130 °C	Linear Eq.	$y = 4.79 - 0.67x$	$y = 4.41 - 0.64x$	$y = 4.28 - 0.56x$
	n	0.33	0.36	0.44
	K	61659.50	25704.00	19054.61
140 °C	Linear Eq.	$y = 4.66 - 0.70x$	$y = 4.26 - 0.59x$	$y = 4.13 - 0.51x$
	n	0.30	0.41	0.49
	K	45708.82	18197.00	13489.63
150 °C	Linear Eq.	$4.51 - 0.71x$	$y = 4.22 - 0.65x$	$y = 4.06 - 0.54x$
	n	0.29	0.35	0.46
	K	32359.37	16595.87	11481.54
ΔE_η ($x = 0$)	(kJ/mol)	45.67	32.78	36.01

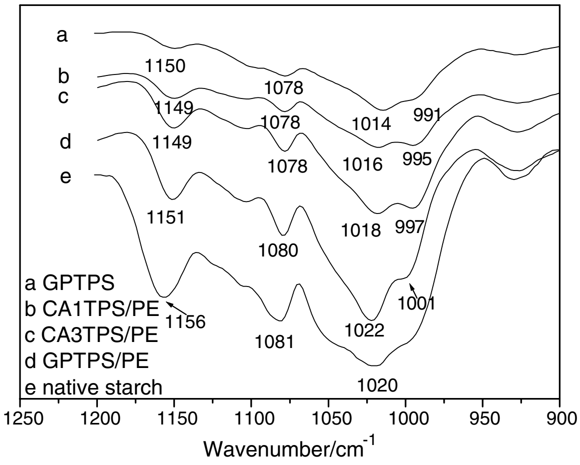

Fig. 4. FT-IR spectra of native starch and TPS in different TPS/PE blends.

bond stretching, and the peak at about 1018 cm^{-1} was a characteristic peak of the anhydroglucose ring O–C stretch (Fang, Fowler, Tomkison, & Hill, 2002).

There were many reports that use FT-IR to study the compatibility of TPS/PE blends containing compatilizer such as EAA, MAH and so on. CA made starch partial acidolysis and reduced the molecules as well as. Granular starch was destructured, plasticized, melted but also partially depolymerized, at the same time it transformed the semicrystalline granule into a molecular net through combining with plasticizer (glycerol) with hydrogen bonds, rather amorphous material with the destruction of hydrogen bonds between the macromolecules.

The analysis of FT-IR spectra of the blends enables the hydrogen bond interaction to be identified (Pawlak & Mucha, 2003; Yu et al., 2005). On the basis of the harmonic oscillator model the reduction in force constant Δf could be represented by following equation.

$$\Delta f = f_p - f_{np} = \frac{\mu(v_p^2 - v_{np}^2)}{4\pi^2}, \tag{3}$$

where $\mu = m_1m_2/(m_1 + m_2)$ 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 non-plasticized and plasticized oscillators, respectively. The reduction of the force constant brought about by some interaction was directly related to the frequency (or wavenumber) shift of stretching vibrations. Thus, the lower the peak frequency the stronger is the interaction (Pawlak & Mucha, 2003). The characteristic peak of TPS in the blends had been concluded in Table 3.

As shown in Table 3, the characteristic peak of starch near 1160 cm^{-1} was ascribed to the C–O bond stretching of the C–O–H group, where the peak was shifted from 1156 to 1151 m^{-1}, in TPS, GPTPS/PE and CATPS/PE blends. This illustrated that the OH group of starch took part in the hydrogen bond formation. Another two peaks at 990 and 1020 cm^{-1} were attributed to C–O bond stretching of the C–O–C group in the anhydroglucose ring (Pawlak & Mucha, 2003). Here, double peak (Figs. 4a, c–e) appeared instead of the single peak of native starch (Fig. 4b). The hydrogen in the hydroxy group of glycerol could form stable hydrogen bonds with the oxygen in the C–O–C group of starch, while the hydrogen bond interacted between glycerol and the oxygen of the C–O–C group of the starch was strengthen even than TPS in the present of CA, and both the peak style and situation changed less (Figs. 4b and c). So it is certain that the hydrogen bond between TPS and glycerol was strengthened in the presence of CA.

3.5. X-ray diffractometry

Native cornstarch existed in semicrystalline granules, being mostly polyhedral in shape and characterized by

Table 3
The wavenumber related to the groups of hydrogen bond in FT-IR spectrum and the change of the force constant Δf

TPS/PE	The vibration wavenumber (cm^{-1})			
	C–O of C–O–H in starch		C–O of C–O–C in starch	
Native starch	1156	1081	1020	
GPTPS	1150	1078	1014	991
GPTPS/PE	1151	1080	1022	1001
CA1TPS/PE	1149	1078	1018	997
CA3TPS/PE	1149	1078	1016	995

almost perfect left-handed, sixfold double helices which were known as A-type spectrum (van Soest, Hulleman, de Wit, & Vliegenthart, 1996). Compared to native cornstarch, the crystal behavior of TPS changed much. Because the intermolecular and intramolecular hydrogen bonds in starch were destructed by plasticizers and other additives in the processing. Therefore, crystalline starch was converted to a dispersed, essentially amorphous, homogeneous material. As shown in Figs. 5B and C, no obvious crystals in both GPTPS and CA2TPS could be observed.

The diffraction scans for TPS/PE blends were also examined (shown in Fig. 6). Both samples had three main crystalline diffraction peaks at 2θ of 21.28°, 23.58° and 29.06°, corresponding to the 110, 200, 210 lattice planes of the orthorhombic crystalline form of polyethylene. These results showed that the crystalline form of PE did not change much after being blended with starch and glycerol. However, the interplanar distance of the TPS/PE was a little higher than that of PE (see Table 4), which meant that the order of macromolecules arrangement in crystalline lattices of PE was slightly affected. But in the presence of CA, this change in the TPS/PE blends was minimized. This might ascribe to the high dispersion between TPS and PE in the presence of CA. A typical A-type spectrum of starch scattering centered at 2θ of 19.46° was found only in the GPTPS/PE blends, but it was not found in CATPS/PE

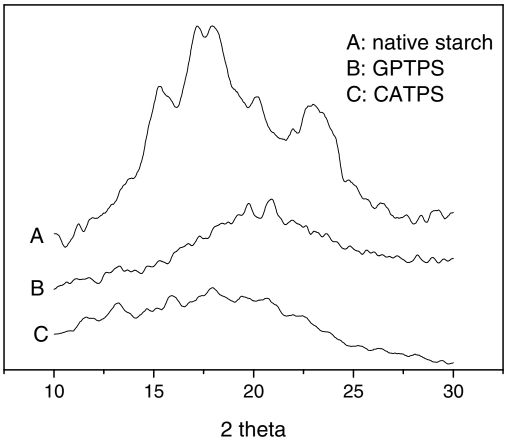

Fig. 5. The X-ray diffraction patterns of native starch, GPTPS and CATPS.

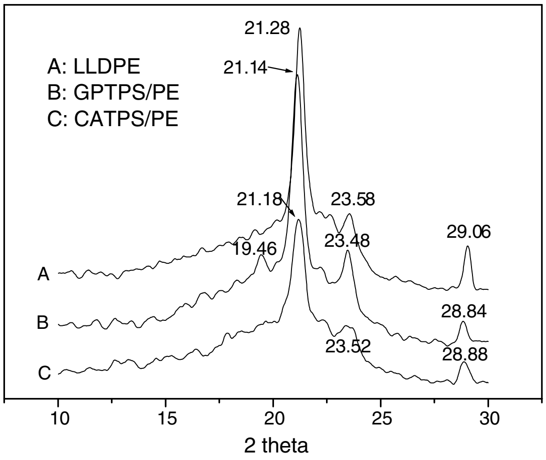

Fig. 6. The X-ray of LLDPE and GPTPS/PE, CATPS/PE blends.

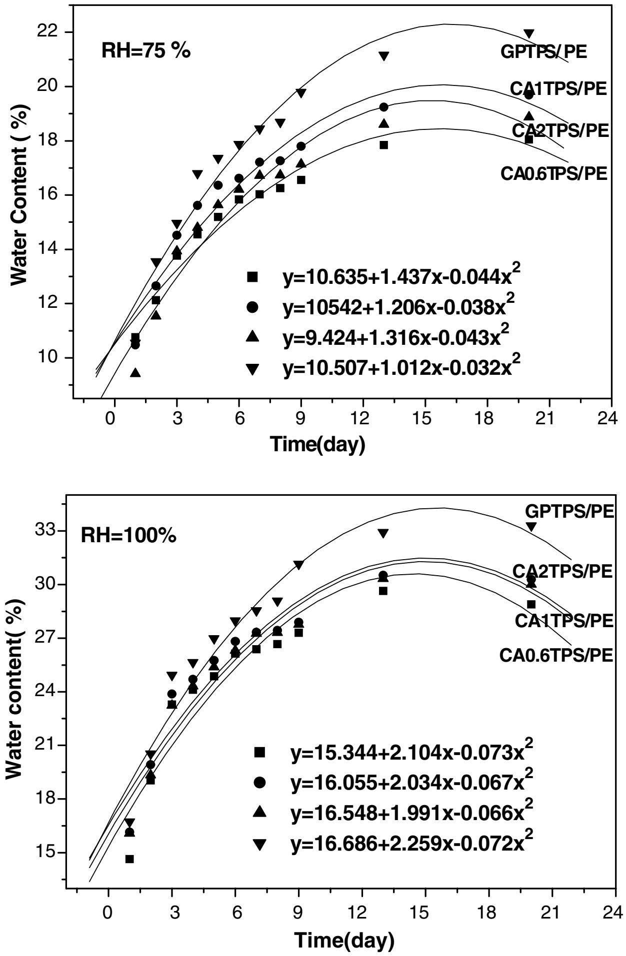

Fig. 7. The water sorption of GPTPS/PE and CATPS/PE.

Table 4
d-Spacing of crystal planes from X-ray of LLDPE and GPTPS/PE, CATPS/PE blends

Sample	110		200		210	
	2θ	Interplanar distance, d_{hkj} (Å)	2θ	Interplanar distance, d_{hkj} (Å)	2θ	Interplanar distance, d_{hkj} (Å)
LLDPE	21.28	4.1757	23.58	3.7734	29.06	3.0939
GPTPS/PE	21.14	4.2031	23.48	3.7892	28.84	3.0960
CATPS/PE	21.18	4.1952	23.52	3.7829	28.88	3.0919

blends. This also supported that non-polar PE deteriorated the plasticization of starch in one-step extrusion.

3.6. Storage conditions and water contents

Water sensitivity was another important criterion in many practical applications of TPS/PE blends. Fig. 7 showed the relation of water contents in TPS/PE blends with different CA contents and storage time at RH = 75% and 100%. Polynomial non-linear regression equations for water contents and the relative equilibrium time were obtained in Fig. 7. The equilibrium water content of GPTPS/PE was, respectively, about 20.1% and 32.5% at RH = 75% and 100%, while the equilibrium water content of CATPS/PE varied with CA contents from 19.6% to 18.5% at RH = 75% and from 30.3% to 28.8% at RH = 100%. After blending with PE, the water resistance of TPS/PE blends was improved (Yu et al., 2005). The addition of CA could also improve the water resistance of TPS/PE blends at high relative humidities, however, the equilibrium water content of CATPS/PE blends varied little when CA contents increased from 0.6% to 3%.

4. Conclusion

The properties of TPS/PE blends were dramatically increased by using a small amount of citric acid as additives in glycerol/starch/LLDPE blends during one-step extrusion processing. It was a novel and promising way to prepare starch-based plastic materials. Compared with other additives such as anhydrides (Bikiaris et al., 1998) or diisocyanates (Jun, 2000) in starch-based plastic materials, CA was a non-toxic and non-volatile additive. So this material could be safely applied in food packaging and other fields. Work about CA as additives in biodegradation materials/starch would be continued.

References

Bikiaris, D., Prinos, J., Koutsopoulos, K., Pavlidou, E., Frangis, N., & Panayiotou, C. (1998). LDPE/starch blends containing PE-g-MA copolymer as compatibilizer. *Polymer Degradation and Stability, 59*(1–3), 287–291.

Carvalho, A. J. F., Zambon, M. D., Curvelo, A. A. S., & Gandini, A. (2005). Thermoplastic starch modification during melt processing: hydrolysis catalyzed by carboxylic acids. *Carbohydrate Polymer, 62*(4), 387–390.

Fang, J. M., Fowler, P. A., Tomkison, J., & Hill, C. A. S. (2002). The preparation and characterisation of a series of chemically modified potato starches. *Carbohydrate Polymer, 47*(3), 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.

Jun, C. L. (2000). Reactive blending of biodegradable polymers: PLA and starch. *Journal of Polymers and the Environment, 8*(1), 33–37.

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.

Ma, X. F., & Yu, J. G. (2004). The plasticizers containing amide groups for thermoplastic starch. *Carbohydrate Polymer, 57*(2), 197–203.

Pawlak, A., & Mucha, M. (2003). Thermogravimetric and FTIR studies of chitosan blends. *Thermochimica Acta, 396*(1-2), 153–166.

Pei-xi, W., & Liu-cheng, Z. (1996). *Polymer blending*. Beijing: Chinese Light Industry, 151.

Rodriguez-Gonzalez, F. J., Ramsay, B. A., & Favis, B. D. (2003). High performance LDPE/thermoplastic starch blends: a sustainable alternative to pure polyethylene. *Polymer, 44*(5), 1517–1526.

Stepto, R. F. T. (2003). The processing of starch as a thermoplastic. *Macromolecules Symptoms, 201*, 203.

van Soest, J. J. G., Hulleman, S. H. D., de Wit, D., & Vliegenthart, J. F. G. (1996). Crystallinity in starch bioplastics. *Industrial Crops and Products, 5*(1), 11–22.

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.

Willemse, R. C., de Posthuma, B. A., van Dam, J., & Gotsis, A. D. (1998). Co-continuous morphologies in polymer blends: a new model. *Polymer, 39*(24), 5879–5887.

Willett, J. L. (1994). Mechanical properties of LDPE/granular starch composites. *Journal of Applied Polymer Science, 54*(11), 1685–1695.

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

Yu, J. G., Wang, N., & Ma, X. F. (2005). The effects of citric acid on the properties of thermoplastic starch plasticized by glycerol. *Starch, 57*(10), 494–504.