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Characterization of citric acid/glycerol co-plasticized thermoplastic starch prepared by melt blending

Rui Shi [a], Zizheng Zhang [a], Quanyong Liu [a], Yanming Han [a],
Liqun Zhang [a,*], Dafu Chen [b,*], Wei Tian [c]

[a] The Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China
[b] Laboratory of Bone Tissue Engineering of Beijing Research Institute of Traumatology and Orthopaedics, Beijing 100035, People's Republic of China
[c] Department of Spine Surgery of Beijing JiShuiTan Hospital, The Fourth Clinical Medical College of Peking University, Beijing 100035, People's Republic of China

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Abstract

A novel citric acid (CA)–glycerol co-plasticized thermoplastic starch (CGTPS) was prepared by melt blending. The CA content varies from 10% to 40 wt%. Result from Fourier Transform Infrared spectroscopy (FTIR) show that partial esterification occurred during blending. The degrees of substitution and esterification increased as the CA content increased. Results from intrinsic viscosity measurement, laser light scattering (LLS), and FTIR demonstrate the molecular weight of starch decreased as the CA percentage increased. The weight average molecular weight (M_w) of CGTPS with 20 wt% CA was only one-tenth of that without CA under the same processing conditions. Crystal type and crystallinity changes as a function of CA were recorded by X-ray diffraction (XRD). Thermal stability and the glass transition temperature (T_g) were detected by thermogravimetric (TG) and differential scanning calorimeter (DSC). Compared to the traditional GTPS, the novel CGTPS exhibits the special characters of partial esterification, low molecular weight and stronger interaction between starch and plasticizers. These new properties can be expected to prevent retrogradation, promote compatibility with polyesters, improve the processing ability, and adjust the degradation properties.

Keywords: Corn starch; Citric acid; Glycerol; Thermoplastic; Melt blending

1. Introduction

Starch is an important productive polysaccharide in plants. Because of its low cost, availability as a renewable resource, biodegradable and the innocuous degradation products, it has already been widely researched as an important raw material for environment and biomedical applications.

Native starch, which occurs as isolated granules, is partially crystalline, with a crystallinity of 20–45% (Zobel, 1988). There are many hydrogen bonds between the starch macromolecules, which reduce the movement of these molecules, so the native starch has poor processing ability. Thermoplastic starch (TPS) can be obtained by destruction of the granules in the presence of plasticizers under specific conditions. Polyols are the most widely used plasticizers, such as glycerol (Fishman, Coffin, Konstance, & Onwulata, 2000; Shi, Liu, & Tian, 2006), glycol (Smits et al., 2001; Yu, Gao, & Lin, 1996), sorbitol (Wang, Shogren, & Carriere, 2000) and sugars, of these glycerol is the most commonly used plasticizer. However, glycerol plasticized thermoplastic starch (GTPS) can recrystallize (retrogradate) on storage. In order to prevent retrogradation, some plasticizers containing amide groups were used, such as formamide and acetamide (Ma & Yu, 2004a, 2004b), urea (Ma & Yu, 2004a) and the formamide/urea (Ma, Yu, & Feng, 2004) mixture. However, these amide group

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[*] Corresponding authors.
E-mail address: shirui@stud.buct.edu.cn (R. Shi).

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containing plasticizers are toxic, and would not be allowed in many applications, such as fast food service-ware, food packaging, pharmacy, biomedical application.

To resolve this problem, a nontoxic plasticizer which will prevent retrogradation is required. CA is rated as nutritionally harmless compared to other substances used for derivatization. It is a nontoxic metabolic product of the body (Krebs or citric acid cycle), and has already been approved by FDA for its use in humans (Yang, Webb, & Ameer, 2004). Compared with glycerol, the carboxyl groups on citric acid can form stronger hydrogen bonds with the hydroxyl groups on starch molecules, so as to promote the ageing resistant ability, which have already been demonstrated under the low CA content (from 0.6 to 2 wt%) by Yu, Wang, and Ma (2005). However, there is no information available on the properties of the CGTPSs when high levels CA are introduced. In particular, the chemical changes to the starch molecules as a function of CA have not been studied yet. In this study, the CA percentage was increased to as much as 10–40 wt%.

Partial esterification may occur during the melt blending, resulting in some new properties. The groups introduced into the starch chains by esterification are capable of disrupting inter- and intra-molecular hydrogen bonds. The decrease in interactions among the starch molecules can prevent retrogradation (Seow & Thevamalar, 1993). CA will act as a plasticizer. One part of CA that reacts with starch can be considered as an internal plasticizer, while the other part of CA plays a role as an external plasticizer. Moreover, some new groups (carboxyl groups and ester groups) will be introduced into the starch molecules. The carboxyl groups not only change the properties of the material, but also supply the potential reactive points for modification by grafting and cross-linking. The ester groups may improve the compatibility with some other biodegradable polyester.

There are many kinds of esterified starch, such as starch acetate (with vinyl acetate), starch phosphate (with orthophosphates), carboxymethyl starch (with monochloro acetic acid), and starch citrate (Singh, Kaur, & McCarthy, 2007). Compared to other preparation methods, melt blending is an easier way for large-scale industrialization. However, starch acetates were always prepared in aqueous suspensions for a few hours (Billmers & Tessler, 1993). A more rapid method for preparing the starch acetate of intermediate degree of substitution (DS 1.0–2.5) was suggested by Shogren (1996). In their work, the starch acetates can be obtained by melt blending of native starch with acetic anhydride in the presence of alkaline catalyst for a few minutes. The citrate starches were always produced using a dry reaction method by reacting starch with citric acid at elevated temperature for more than 3 h according to Klaushofer et al. (Klaushofer, Berghofer, & Steyrer, 1978; Wepner, Berghofer, Miesenberger, Tiefenbacher, & Ng, 1999; Xie & Liu, 2004; Xie, Liu, & Cui, 2006). Although, Carvalho and his coworkers prepared the glycerol/carboxylic acids co-plasticized starch by melt blending (Carvalho, Zambon, Curvelo, & Gandini, 2005), the carboxylic acids content (0.5–3%) in their study was far lower than ours (10–40%). so some special properties were not displayed under such low CA content. Moreover, their emphasis was focused on the effects of carboxylic acids on the starch molecular weight. However, the other effects of the citric acid were not mentioned.

A decrease in starch molecular weight might be expected to occur through acid hydrolysis due to the presence of CA. However, the relationship between the molecular weight and the CA content during processing has not been reported yet, as well as the effect of the low molecular weight on the thermal stability and crystal structure.

In the present study, the CA (10–40 wt% based on the wet starch) and glycerol were used as the co-plasticizers. The properties of the CGTPS were investigated. The chemical changes of the starch molecules as the function of CA content were studied. The aim is to obtain a novel thermoplastic starch with the properties of partial esterification, low molecular weight and strong interaction between starch and plasticizers. The new properties may have some benefits to prevent ageing, to promote the processability, to adjust the biodegradation speed, and to improve the compatibility and distribution when blended with polyester.

2. Experimental

2.1. Materials

Corn starch was supplied by J&K Chemical Ltd. (Japan), which is composed of 25% amylose and 75% amylopectin. The original moisture content was 12 wt%. The glycerol (AR) was obtained from Century Star Chemical Products Inc. (Beijing, China). Citric acid (AR) was supplied by Xu Dong chemical plant (Beijing, China), and dimethyl sulfoxide (DMSO, AR) was obtained from the Beijing chemical plant (Beijing, China).

2.2. Preparation

The water content of corn starch was adjusted to 20 wt% (wet base) by addition of distilled water. Glycerol and water were mixed first, and then blended with corn starch by use of High Speed Mixer GH-100Y (made in China). When CA was used, it was firstly dissolved in the additional water. The mixture was sealed and stored overnight. The ratio of glycerol to corn starch (w/w) was 30:100. The abbreviations for the different samples prepared and their compositions are listed in Table 1. The melt blending procedure was performed in the Haake Rheomix (Thermal Electron Co., USA) at 130 °C at 80 rpm for 13 min.

2.3. Characterizations

2.3.1. Fourier transforms infrared (FTIR) spectroscopy

The IR spectra were measured with a Nicolet-210 spectrophotometer (Nicolet Co., USA). The samples were

Table 1
Materials' abbreviations and corresponding sample compositions

Materials	Abbreviations	Samples (weight proportions)		
		Hydrous starch (20 wt% water content)	Glycerol	CA
GTPS	CA0	100	30	0
CGTPS1	CA1	100	30	10
CGTPS2	CA2	100	30	20
CGTPS3	CA3	100	30	30
CGTPS4	CA4	100	30	40

prepared by mixing the fine powder with KBr and pressing. The CGTPS had been dipped in excess de-ionized water to remove the residual CA before the test. The spectra were obtained at a resolution of 4 cm^{-1} in the range 4000–500 cm^{-1}.

2.3.2. X-ray diffraction (XRD)

The wide-angle XRD patterns of products were recorded with a Rigaku model D/Max2500VB2+/PC X-ray diffractometer (Japan) with nickel filtered Cu-Kα radiation. The samples were 1 mm thickness with smooth surface. The scattering angles (2θ) ranges were from 3° to 60° at 5° min^{-1}.

2.3.3. Differential scanning calorimeter (DSC)

Differential scanning calorimetry (DSC) thermograms were recorded by a NETZSCH DSC 204 F1 (Germany) instrument. The sample (3–10 mg) placed in aluminium pan was firstly cooled from room temperature to −150 °C and hold there for 3 min. Subsequently, a heating scan was conducted from −150 to 150 °C at a heating rate of 20 °C/min. The glass transition temperature was taken as the midpoint of the heat capacity change.

2.3.4. Thermogravimetric (TG) analysis

Thermogravimetry analyses were carried out by a NETZSCH TG 209C (Germany) instrument. About 10 mg sample was positioned in silica pans, and the samples were heated at 10 °C/min from ambient temperature to 600 °C. Thermal analyses were performed under a nitrogen purge (10 mL/min).

2.3.5. Laser light scattering (LLS)

The light-scattering intensities of the starch solution were determined with a multiangle LLS instrument ($\lambda = 532$ nm; Brook Haven 200-SM, Brookhaven Instruments Co., USA) at angles from 30° to 150° at 15° intervals. The solvent is the mixture of DMSO and water (w/w, 9:1). The calibration of the laser photometer was done with ultrapure toluene. The optical clarification of the polysaccharide solution and solvent was achieved by filtration through a Millipore filter (0.22 μm). The values of dn/dc were determined using an interferometric refractometer at 532 nm 25 °C. The dn/dc value was determined as 0.300 mL/g.

2.3.6. Inherent viscosity

Viscosity of the CGTPS sample with concentration of 4 g/dL in DMSO was measured by an Ubbelodhe viscometer at 40 °C, and the intrinsic viscosity ($[\eta]$) of the polymer was calculated according to the Eq. (1).

$$[\eta] = \frac{\sqrt{2(\eta_{\mathrm{sp}} - \ln \eta_{\mathrm{r}})}}{c} \tag{1}$$

Where $\eta_{\mathrm{r}} = \eta_{\mathrm{t}}/\eta_0$ and $\eta_{\mathrm{sp}} = \eta_{\mathrm{r}} - 1$; η_{t} and η_0 are the viscosities of polymer solution and solvent, respectively. c is the concentration of the solution.

Eq. (1). can be obtained from Eqs. (A) and (B)

$$\frac{\eta_{\mathrm{sp}}}{c} = [\eta] + k'[\eta]^2 c \tag{A}$$

$$\frac{\ln \eta_{\mathrm{r}}}{c} = [\eta] + \beta[\eta]^2 c \tag{B}$$

Eq. (A) minus Eq. (B):

$$\frac{\eta_{\mathrm{sp}}}{c} - \frac{\ln \eta_{\mathrm{r}}}{c} = (k' + \beta)[\eta]^2 c \tag{C}$$

k' and β are all constants, When $k' + \beta = \frac{1}{2}$, Eq. (1) can be obtained.

Eq. (1) is an approximate equation for the intrinsic viscosity based on one point. Eq. (1) is valid when $k' + \beta = \frac{1}{2}$, or $k' \approx 0.3$–0.4. Generally, this equation is applicable for linear flexible polymers in good solvents. In order to satisfy these conditions, η_{r} is always controlled in the range of 1.2–2.0. For all work the concentration was 4 g/dL.

2.3.7. Degree of substitution (DS) and esterification (ED)

The DS and ED were determined according to Santayanon and Huang (Huang, Xiao, Zheng, & Huang, 2004; Santayanon & Wootthirahokkam, 2003). Before the test, the plasticizers such as the glycerol and residual citric acids in the samples have been removed by water extraction, so the effects of the plasticizers on the DS and ED can be neglected. The NaOH and HCl volumetric solutions were prepared according to GB/T601-2002 which is a Chinese standard for preparations of standard volumetric solutions. The sample of starch citrate was dissolved in DMSO solution in a conical flask and then excess NaOH was added to the solution to saponify the ester. The excess NaOH was determined by titration with the calibrated HCl. Phenolphthalein was chosen as the indicator. The following Eq. (2) was used to determine the ED:

$$\mathrm{ED} = [V_{\mathrm{NaOH}} \times N_{\mathrm{NaOH}} - V_{\mathrm{HCL}} \times N_{\mathrm{HCl}}] \times M \times 100/m \tag{2}$$

Where V_{NaOH} and V_{HCL} are the volumes (L) of the NaOH solution and HCl solution, and N_{NaOH} and N_{HCl} are the molar concentrations (mol/L) of them. M is the weight addition of one glucose ring unit which was substituted by the CA, and the value of M is 174 (g/mol). m (g) is the weight of the sample.

The degree of substitution was calculated according to Eq. (3)

$$\mathrm{DS} = 162 \times A/(1 - M \times A) \tag{3}$$

Where A is the mole number of the NaOH solution which was reacted with 1 g substitute; 162 is the molecular weight of the glucose ring unit.

3. Results and discussion

3.1. Chemical structure changes

3.1.1. Partial esterification of the starch chains

Fig. 1 shows the FTIR spectra of GTPS, pure CA, and CGTPSs with different CA contents. The wave number ranges are from 2000 to 1500 cm^{-1}(Fig. 1(a)) and 1200 to 800 cm^{-1} (Fig. 1(b)). We noticed that a broad peak at 1729 cm^{-1} appeared on the spectra of CGTPSs but can not be found on those of the GTPS and pure CA. The broad peak at 1729 cm^{-1} is the C=O stretching vibration peak, and it is probably a coalescence peak which is caused by the ester bond and carboxyl C=O groups in citric acid, because it is unlikely that all the carboxyl groups are esterified. However, the peak at 1709 cm^{-1} which is attributed to the C=O stretching vibration in carboxyl groups was only found on the FTIR spectra of pure CA. The peak between 1750 and 1800 cm^{-1} is an interference peak which can be found when the carboxyl groups are very close to each other in diacid or polyatomic acid (Xie, Chang, & Wang, 2001) The change of the peak's position from 1709 cm^{-1} in pure CA to 1729 cm^{-1} in CGTPSs demonstrated that the ester bonds existed in CGTPS, and the esterification reaction between starch and CA happened in the course of melt blending.

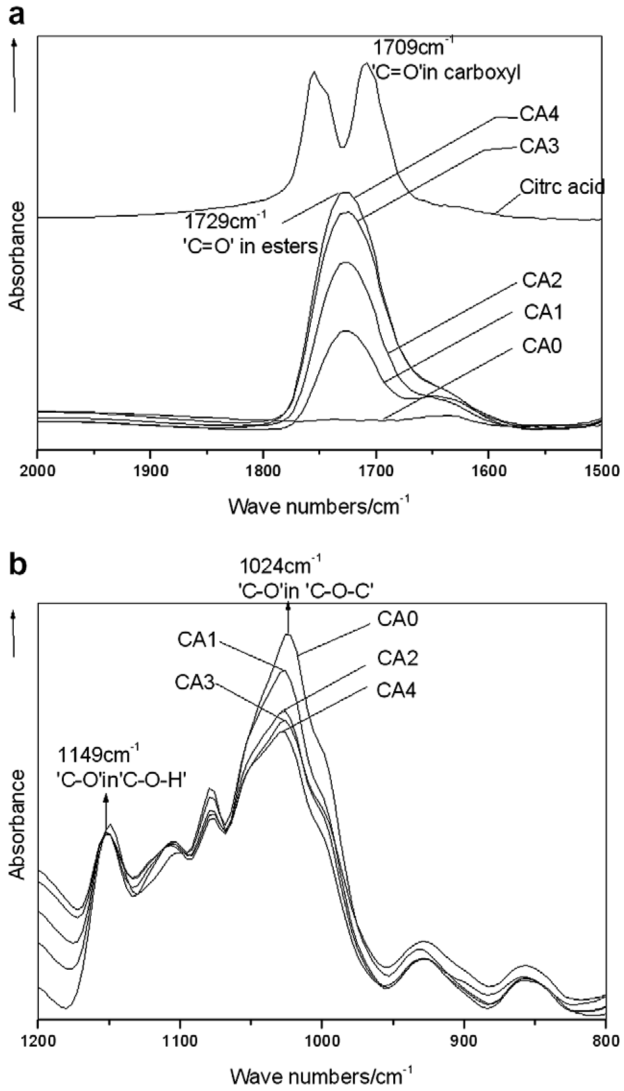

Fig. 1. Comparison of the FTIR spectra of different CGTPSs with different CA content.

Before the FTIR test, the residual citric acids in the samples have been removed by the water extraction method, so the influence of the CA had already been eliminated. Although there are some unesterified carboxyl groups in the system, however, the unesterified carboxyl groups increased as the ester bonds increased. Therefore, the increase of the peak's height at 1729 cm^{-1} can also reflect the increase of the ester bonds. The comparison of peak heights at 1729 cm^{-1} of different CGTPSs was also shown in Fig. 1(a). When a 'C–O–H' on the starch was reacted with a CA molecular to form a 'C–O–C', the starch would have a new 'C–O–H' supplied by the CA, as a result, the total number of 'C–O' bonds in 'C–O–H' groups were considered to be the same. Therefore, when the other peaks' heights were discussed, the stretching vibration peak of 'C–O' in 'C–O–H' group at 1149 cm^{-1} (Yu et al., 2005) was chosen as the reference peak. The peak heights were measured from the baseline, which passed through the lowest point of the spectra and parallel to the x-axis. It can be seen from Fig. 1(a) that the peak's height at 1729 cm^{-1} increased as the CA percentage increased.

Results from FTIR suggest that the esterification happened during melt blending, and the ED increased as the CA percentage increased. The esterified citric acids which were bound to the starch chains are capable of disrupting the inter- and intra-molecular hydrogen bonds. The free carboxyl groups attached to esterified citric acid could also increase solubility of starch and prevent crystallization. This can be supported by the results of the FTIR and XRD from Yu and his coworkers study (Yu et al., 2005). In their work, the XRD curves of the CGTPS with a small amount of CA change insignificantly over 70 days.

Because the motional freedom of starch chains in amorphous regions increased as the hydrogen bonds decreased, the CA reacted with starch can be considered as the internal plasticizer, while the residual CA in the blends plays the role of external plasticizer. Moreover, the esterification can also change the groups on the starch chains. Some new groups (carboxyl groups and ester groups) were introduced onto the starch molecules, which can supply the potential reactive points for the modification by grafting and cross linking.

Table 2
Degrees of substitution and esterification of CGTPS with different CA contents

Symbols	CA1	CA2	CA3	CA4
ED/%	9.801	16.33	19.10	21.56
DS/%	0.101	0.182	0.220	0.256

In order to have a further investigation on partial esterification, DS and ED were tested by titration. The results were listed in Table 2. ED is the percentage of the reacted hydroxyl groups in the total hydroxyl numbers. DS is expressed as the average number of moles of substituent per anhydroglucose unit. As each anhydroglucose unit has three hydroxyl groups available for substitution, the maximum possible DS is 3 (Singh et al., 2007). This result shows that the ED and DS are increased as the CA content increased under the same temperature and reaction time. We noticed that when the CA content reached as much as 20 wt%, the increase of the CA content has less effect on the ED and DS.

We can see that the ED and DS of CA4 reached as much as 21.6% and 0.256%, respectively, and the DS has reached the medium substitution degree of the starch acetate (0.2–2). Moreover, compared to the traditional methods, the direct melt blending is an easy way to produce the esterification starch, which can greatly reduce the reactive time and procedure.

3.1.2. Decrease of the molecular weight

The result from FTIR also illustrates the decrease in molecular weight caused by the starch chain breakage with increasing of CA. The peak at 1024 cm^{-1} is attributed to the stretching vibration of 'C–O' in 'C–O–C' (Fang, Fowler, Tomkinson, & Hill, 2002) (see Fig. 1(b)). The peaks' height at 1024 cm^{-1} decreased as the CA content increased, and the peaks of CGTPSs are all lower than those of GTPS. The stretching vibration peak of 'C–O' in 'C–O–H' group at 1149 cm^{-1} was selected as the reference peak again. The decrease of the peak height was caused by the decrease of the 'C–O–C'. The reason may be that the higher the CA content the greater the acid hydrolysis of the glycosidic linkages.

The effect of the CA content on molecular weight can be obtained from the empirical Mark-Houwink equation: $[\eta] = kM^{\alpha}$ (Where k and α are the Mark-Houwink constants), the change of the intrinsic viscosity reflects the variation of the molecular weight. Fig. 2 shows the comparison of the intrinsic viscosities of native starch, GTPS and CGTPSs.

Compared to native starch, the intrinsic viscosity values of GTPS decreased, which may be caused by the breakage of the starch molecules under the heat and the shear force during the processing procedure. Moreover, compared with GTPS, the inherent viscosity values of CGTPSs decreased much more, which can be attributed to the hydrolysis of the starch chains. It can be clearly seen that the intrinsic viscosity values reduced as the CA contents increased. It was also observed that the decrease was significant when the CA content increased above 20%. However, when the content went up to 20%, increase of the percentage of CA had little effect on the intrinsic viscosity. So we detected the weight average molecular weights (M_w) of GTPS and CGTPS with 20 wt% CA content by static laser light scattering (LLS). The values of the inherent viscosity and M_w were listed in Table 3. The M_w of the thermoplastic starch without CA is $(1.48 \pm 0.19) \times 10^6$ g/mol, but the M_w of the CGTPS with 20 wt% CA is $(1.85 \pm 0.87) \times 10^5$ g/mol, which is only about one tenth of that of the GTPS. All the above results clearly showed that the addition of CA decreased the molecular weight a lot. This result is consistent with the results obtained by Carvalho and his coworkers [Carvalho et al., 2005]. However, we noticed that the M_w of the CGTPS with 2 wt% CA content in their work was only 0.078×10^6 g/mol, which was smaller than that of CGTPS with 20 wt% CA content in our study. We noticed that the plasticizing temperature in their work was 160 °C, which was higher than that used in our study (130 °C). This illustrate that the starch chains can be broken down more easily by CA at the high temperatures than at low temperatures.

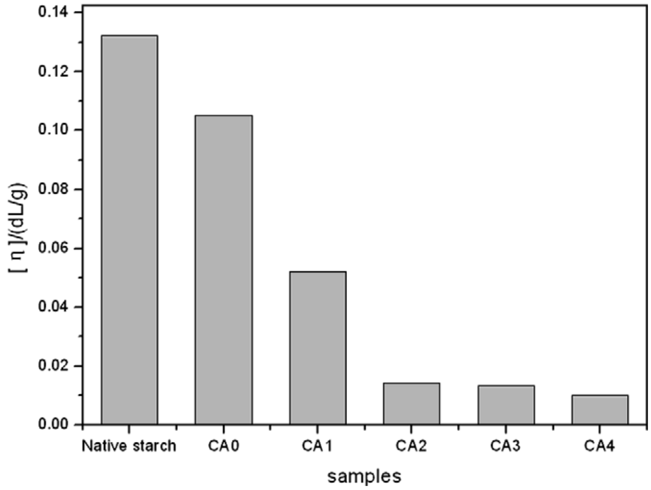

Fig. 2. The effect of the citric acid content on the intrinsic viscosity.

3.2. Thermal properties changes

3.2.1. Thermogravimetric (TG) analysis

Fig. 3 shows the thermogravimetic curves of GTPS and CGTPS with different CA contents. The weight loss below 100 °C was mainly caused by water evaporation, and the weight loss above 100 °C to both the evaporation of water and other plasticizers and thermal decomposition of the starch. Therefore, the differences in the onset temperatures of starch thermal decomposition and weight loss at onset temperature were mainly due to the type and content of the plasticizers. It seems that there is only one weight loss step on the TG curve of GTPS, but two steps on the curves

Table 3
Effects of the citric acid on the inherent viscosity[η] and weight average molecular weight (M_w)

	Native starch	CA0	CA1	CA2	CA3	CA4
[η]/($dL \times g^{-1}$)	0.132	0.105	0.052	0.014	0.013	0.010
M_w/($g \times mol^{-1}$)	–	$(1.48 \pm 0.19) \times 10^6$	–	$(1.85 \pm 0.87) \times 10^5$	–	–

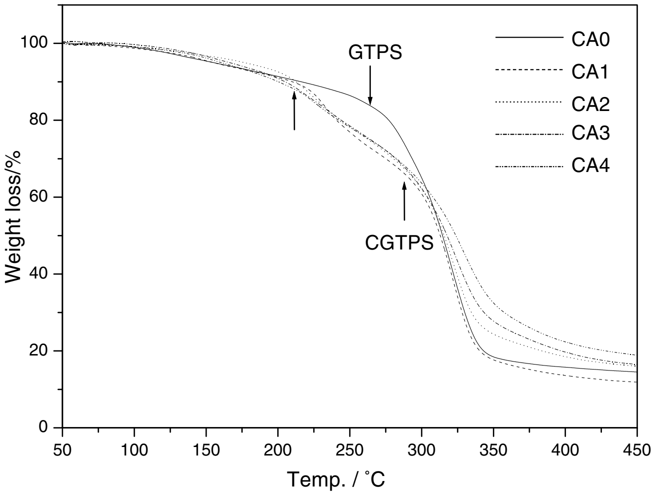

Fig. 3. Thermogravimetic curves of GTPS and CGTPSs.

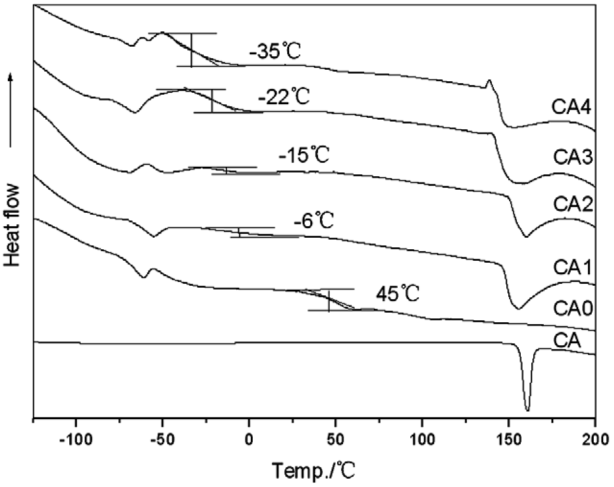

Fig. 4. Comparison of the DSC curves as a function of the citric acid.

of CGTPSs. The first weight loss step that started from 150 °C may be due to the heat decomposition of the residual CA in CGTPS. The second step was mainly caused by the thermal decomposition of the starch chains. The onset temperatures of the second weight loss steps are strongly related to the interactions between plasticizers and the starch. It seems like that the CGTPSs had higher onset temperature and lower mass loss than GPTPS. This indicated that the presence of citric acid increased the binding of plasticizers to starch. In other words, the bonding between the citric acid and starch is stronger than that between glycerol and starch. This result is consistent with what was obtained by Yu et al. (2005).

It can also be seen that the residual weight percentage of the CGTPSs was more than that of the GTPS, and the residual weight percentage increased as the CA content increased. It seems that the addition of the CA enhanced the incarbonization. When the CA content increased, more and more CA molecules were chemical bonded onto the starch chains, so the initial carbon content increased as the esterification occurred. Therefore, the residual weight increased as the CA content increased.

3.2.2. Differential scanning calorimeter (DSC) analysis

Fig. 4 shows the DSC curves of pure CA, GTPS and CGTPS with different CA content. The melting peak that appeared in all curves around −65 °C was attributed to the "glycerol rich phase". This phase is composed of glycerol, water and a small amount of starch molecules (Forssell, Mikkilä, Moates, & Parker, 1997). Another peak around 150 °C that appeared on the curves of CGTPSs may be caused by the melting of the residual CA and the re-crystallized starch. We can see that the melt point of the pure anhydrous CA is 159 °C as shown in Fig. 4, and the starch recrystallization also gives a melting peak in this range (Chung & Lim, 2004).

It can be seen from Fig. 4 that the glass transition temperature (T_g) decreased as the CA content increased. The T_g of GTPS with 30 wt% glycerol content (CA0) was about 45 °C, which was above room temperature. Therefore, CA0 was in the glassy state at and below the room temperature. When 10 wt% CA was added, the T_g was greatly decreased to −6 °C. As the CA percentage increased, the T_g gradually decreased. The T_g of CGTPS with 40 wt% CA dropped to −35 °C. We noticed that all the glass transition temperatures of CGTPS were below 0 °C, so they were soft and flexible under room temperature. The decrease in the T_g may be caused by three reasons. The main cause is that the number of the hydroxyl groups on the starch molecules which can form strong hydrogen bonds between chains decreased. The second is that the increase of the plasticizers made the starch molecules move more mobile. The last reason may be that the molecular weight decreased as the CA content increased. Those shorter molecules after acid hydrolysis have more mobility than the longer ones.

3.3. Crystal structural changes

The crystal structure changes were detected by X-ray diffraction. The X-ray diffraction patterns of pure CA, native starch, GTPS and CGTPSs with different CA content are shown in Fig. 5. It can be seen that the crystal

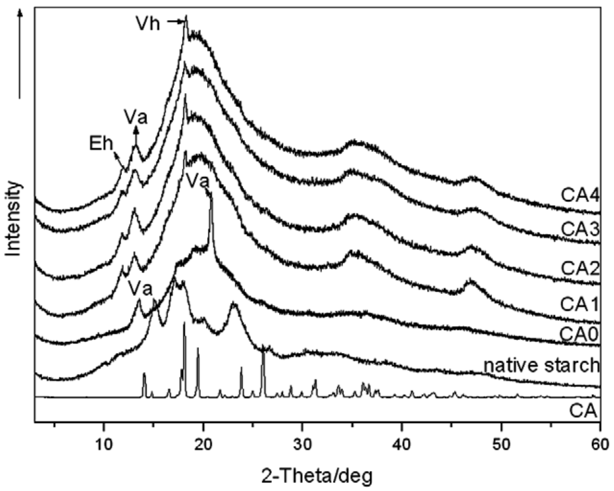

Fig. 5. Comparison of the X-ray diffraction patterns of native starch, GTPS and GTPSs.

peaks of pure CA disappeared on curves of the CGTPSs, which illustrates that the CA dispersed in CGTPS at the molecular level. Compared to the native starch, the crystal types of GTPS and CGTPS changed a lot. The typical crystal peaks of A-type structure of native starch have disappeared from both GTPS and CGTPS (van Soest & Vliegenthart, 1997).

In addition, the crystal type and crystallinity of CGTPS were very different from those of the GTPS. There are two characteristic peaks on the curve of CA0 at 13.2° and 20.8°, which are attributed to the V_a-type crystal structure. However, the peak at 20.8° disappeared on the diffraction curves of CGTPS, meanwhile, two peaks at 18.3° and 11.8° appeared, which were attributed to the V_h- and E_h-type crystal structure (van Soest & Vliegenthart, 1997).

It is considered that the V- and E-type crystals are single helical structures typical of the complexes formed between the amylose and the lipids (i.e., fatty acids) present in cereal starch, which is induced during processing (ex. Extrusion, injection, compression moulding) (Lebaih et al., 1995). It is reported that the V_a- and E_h-type crystals are in the unstable state, and they will translate into V_h-structure gradually on storage (Lebaih et al., 1995; Liu, 2002). When CA was added, the more stable V_h-type structure appeared on the XRD curve, and the metastable V_a- and E_h-type structures disappeared. The reason may be caused by the motion freedom of the starch chains was improved. The increase of the plasticizers' percentage and the reduction in the molecular weight of the starch chains. The mobility of the short chains after acid hydrolysis was better than that of the longer ones, which will result in more stable V_h-type structure.

It can also be seen from Fig. 5 that the addition of the CA will reduce the height of the crystal peak significantly. The result demonstrates that the crystallinity decreased when the CA was added. Furthermore, compared with the GTPS, two obvious amorphous peaks at 35.3° and 46.8° only appeared on the diffraction curves of CGTPSs.

4. Conclusions

The novel CA and glycerol co-plasticized TPS has some new characteristics compared with the traditional glycerol plasticized TPS: namely, partial esterification, low molecular weight, and strong interaction between starch and CA.

The ED and DS increased as the CA content increased, the ED and DS of CA4 reached as much as 21.6% and 0.256%, respectively, and the DS reached the medium substitution degree of the starch acetate (0.2–2). The molecular weight decreased as the CA percentage increased. The intrinsic viscosity did not change so much when the CA percentage was more than 20 wt%. The M_w of CGTPS with 20% CA content decreased to one tenth of that without CA. In addition, the CA enhanced the thermal stability of the material, changed the crystal types and reduced the crystallinity compared with the GTPS.

Partial esterification could have some effect on reducing retrogradation, introducing some new groups onto the starch chains for potential modification, and improving the compatibility with the polyesters. The decrease in the molecular weight can improve the processing properties, adjust the degradation speed of the TPS, and improve the diffusion of the CGTPS in the polyesters. Furthermore, the CGTPS can easily be prepared by melt blending in a short time. All of these special properties would make CGTPS a good candidate in wide field applications. Further investigations are underway to understand the processing and degradation properties of the CGTPS.

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