Ageing of Soft Thermoplastic Starch with High Glycerol Content

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ABSTRACT: In this study, a soft and thermoplastic starch with an improved ageing-resistant property was prepared by melt blending method for a biodegradable biomaterial. The glycerol content varies from 30 to 60 wt %. The aging temperature and humidity of the glycerol-plasticized thermoplastic starch (GTPS) was 37°C and 50 ± 5 RH %, respectively. The retrogradation was characterized by X-ray diffraction (XRD), dynamic mechanical thermal analysis (DMTA), Fourier transform infrared (FTIR), and the stress-strain mechanical properties. The XRD results suggest that high content of glycerol promotes the formation of single helix structure of V-type, but inhibits double helix structure of B-type. Changing of the tan δ, storage modules (E'), and the glass transition temperatures as a function of glycerol content and ageing time was detected by DMTA. FTIR result shows that the shifting speed of the peak of hydroxyl group stretching fell as the glycerol content increased. The glycerol content has no obvious effect on the mechanical properties when it is high enough. Results from all characterizations demonstrate that the ageing speed is closely relative to the plasticizers content. The higher content of glycerol possesses an obviously inhibitory effect on the ageing. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 574–586, 2007

Key words: thermoplastics; ageing; crystal structures; glass transition; FTIR

INTRODUCTION

Starch is an important polysaccharide in plants. Because of its low cost and availability as a renewable resource, it has already been widely researched as a raw material for biodegradable plastics. Native starch, which occurs as isolatable granules, is partially crystalline (semicrystalline), with a crystallinity of 20–45%.[1] There are many hydrogen bonds among the starch macromolecules, which hamper the movement of the starch molecules, so the native starch has a poor processing ability. Thermoplastic starch (TPS) can be obtained by destruction of the granules in the presence of plasticizers under specific conditions. Glycerol and water coplasticized thermoplastic starch (GTPS) is a traditional TPS material.

Glass transition is the most important parameter in determining the mechanical properties of amorphous polymers and in controlling the kinetics of crystallization of amorphous materials. Besides the water content, the glycerol content is another important factor which affects the T_g so much. It was reported by Lourdin et al.[2] that a continuous decrease in T_g was observed as glycerol increases from 0 to 25% under R.H 57% at 25°C and 11% water content, and a decrease in elongation (from 7 to 3%) was also observed as glycerol level increased below 12%. Results are discussed comparing with the well-known "antiplasticization" effect in synthetic polymers such as PVC and PC. Myllärinen et al.[3] also suggested that at low glycerol contents, the interaction between the starch and glycerol resulted in more brittle structure for both polymer networks. Especially the amylopectin film with 10% glycerol was extremely difficult to handle and perform the tensile analysis because of its brittleness. They observed that increase in elongation and a great change in the rheological properties when more than 20% of glycerol was added to amylose, which was caused by phase separation. Furthermore, an investigation in which amylose and maltose were plasticized by glycerol also point out a complex phase separation above 25% glycerol on the basis of dielectric mechanical analysis.[4] The glass transition temperature of the starch-rich phase of thermo-

plastic starches having 30% glycerol and 11% water was detected by Lourdin et al.,[5] which had a value of about 0°C using a Setaram DSC121 and so the plates were stored above 0°C is in a rubbery state. However, at very high plasticizer content (above 50%), the material becomes soft and behaves more like a gel or paste. The influence of the glycerol content on the T_g, the mechanical properties and the crystallinity of such high glycerol content GTPS has not been reported.

The GTPS materials are not at equilibrium and exhibit time-dependent changes in their structure and macroscopic properties, which is associated with ageing. Because the predominantly amorphous products are not at thermodynamic equilibrium, the systems will approach the equilibrium in time.[6] Ageing is that changes over time of the structure and material properties of plastic materials when stored above the glass transition (T_g).[7,8]

The ternary system obtained by plasticizing starch with water and glycerol has seemed to behave in a rather complicated way. There are many factors that affect the ageing processing of the blending system, including the relative humidity of the environment, the plasticizers content, the kinds of the plasticizers, the ratio of the amylose and the amylopectin, the environment temperature, etc. Ageing always affects the glass transition temperature and the crystallinity of the material, which results in the change of the mechanical properties as well as some of the other physical properties.

The starch has the good biocompatibility and biodegradability while the glycerol is nontoxic, so the GTPS is promising to be used as biomaterial. In the past decade, the studies of the application of starch in biomaterial were mainly in bone tissue engineering scaffolds,[9–11] as additive of tissue adhesive agent,[12] and the medicine release agent.[13,14] However, little information has been published concerning the preparation of starch into soft state and the application in soft tissue engineering. So we prepared a kind of soft rubbery GTPS material by plasticizing the cornstarch with high glycerol content. The potential usage of the soft rubbery GTPS may be in soft tissue engineering scaffold, as hemostatic agent, etc. However, the ageing of the GTPS will limit its application as biomaterial. Ageing of starch is one of the most important topics in study, while thermal plastic starch and high plasticized materials have not been frequently studied. Therefore, The purpose of this article is to study the changes of the structures during ageing of GTPS with high plasticizers content under the normal human body temperature (37°C) and a comfortable relative humidity for human being (50 ± 5%), so as to understand the mechanism of the ageing well and to control it under certain conditions of human body. Besides the conclusions proposed by other researchers, some new view-

points about the ageing are given in this article. Our work will be valuable for the application of the GTPS in biomedical application.

EXPERIMENTAL

Materials

The native corn starch was supplied by Jinghuayou Starch (Beijing, China). This starch is composed of 25% amylose and 75% amylopectin (according to iodine binding). The original moisture content was around 12%. The glycerol (AR) was obtained from Century Star Chemical Products (Beijing, China).

Sample preparation and storage conditions

Plasticization of corn starch (12 wt % water content) with glycerol was performed in a Haake Rheomix (Thermal electron Co., Waltham, MA) at 110°C and with 80 rpm for 25 min, until the viscosity had reached a nearly constant value. The glycerol content in the mixtures was 30, 40, 50, and 60 wt % for GTPS30, GTPS40, GTPS50, and GTPS60, respectively. The percentages used are based on the total weight of the starch-glycerol-water systems, respectively. The compound obtained from the melt blending processing was pressed into 1-mm thick transparent slice by compression molding. The slices were immediately put in a sealed environmentally controlled instrument container. The condition inside the container was controlled under 50 ± 5% RH and 37°C.

Water absorption (%)

The original water contents (dry basis) of TPS were determined gravimetrically by drying small pieces at 105°C overnight. Under these conditions, evaporation of the plasticizers was negligible. The current weight was weighted after stored under 37°C and 50 RH % for a predetermined period of time. Its water content was calculated on the basis of its original and current weight.

X-ray diffraction

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, using a 1-mm thick sheet with smooth surface. The scattering angles (2θ) ranges were from 3 to 60° at 5°/min. The height of the peaks was measured from the baseline. The baseline passed through the lowest point of the diffractogram, which paral-

leled to the *x*-axis. For the same glycerol content, the sample we detected was the same one during ageing.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal measurements were performed in the temperature range from –100 to 150°C using a polymer laboratories mechanical thermal analyzer (DMTAV, Rheometyic Scientific, Piscataway, NJ). The specimens used in the experiment had a width of 6 mm and a thickness of 1 mm. The DMTA was used in tensile mode at a frequency of 10 Hz. The heating rate was 3°C/min. The tensile force was reduced at −20°C because of the decreasing modulus of the samples.

Mechanical testing

Specimens, with a shape of dumb-bell shaped, according to ISO/DIS 37-1990 Type 3 specifications (1 mm thickness and 2 mm width) were prepared. Tensile tests were performed in a universal tensile testing machine (CMT4104) equipped with 50 N load cell and operated at a cross-head speed of 10 mm/min. The specimen's elongation was derived from the extensometer separation of 18 mm. The *E* modulus was determined from the initial slope of the stress-strain curve (1–5% strain range of stress-strain curve). Five samples of each product were tested at 21°C and the average value of each quantity was reported. The parameters determined were: elastic modulus (MPa), elongation at break (%), permanent set (%), and shore A hardness (°).

FTIR spectroscopy

The IR spectra were measured with a Nicolet-210 spectrophotometer (Nicolet). The native corn starch sample was prepared by mixing the fine powder starch with KBr and then pressed. The 1.0-mm thick GTPS transparent slices were measured by attenuated total reflection (ATR). The spectra obtained at resolution 4 cm^{-1} in the range 4000–500 cm^{-1}.

Differential scanning calorimeter (DSC)

Differential scanning calorimetry (DSC) thermograms were recorded by Perkin–Elmer DSC (Wellesley, MA). The sample (17–20 mg) placed in aluminum pan was first heated from room temperature to 150°C and held there for 5 min to remove its heating history, and then the cooling scan was recorded from 150 to −120°C at the rate of 10°C/min, subsequently, a second heating scan was conducted from −120 to 150°C at the heating rate of 20°C/min. The glass transition temperatures were taken as the midpoint of the heat capacity change.

RESULTS AND DISCUSSION

Wide angle X-ray diffraction

X-ray diffraction has been used to investigate the changes of crystal type and the changes in crystallinity during ageing in GTPS with different glycerol content. Native starch can be classified into A, B, and C forms. Native A- and B-type crystal lattices consist of double helical, six-fold structures.[15,16] The difference between A- and B-type crystallinity is the packing density of the double helices in the unite cell. The B-type structure is described as a more loosely packed hexagonal assembly of the helices with a column of water molecules present in the center of the hexagonal arrangement, whereas in the A-type structure, this column of water is replaced by a double helix.[15,17,18] The C-type structure is thought to be an intermediate structure of the A- and B-type.[19]

A widely accepted model of a typical cereal starch granule involves alternating amorphous and crystalline lamellae, in which the two main components, amylose and amylopectin, are embedded. Amylose is α-(1→4)-D-glucopyranosyl polymer with linear molecules. The residues in amylopectin are α-(1→4)-D-glucopyranose units with α-(1→6) linkages at intervals of ∼ 20 units, depending on the source.[19] When the starch granules are destructed by heat and shear force during processing, amylose, an essentially linear polymer will dissociate out of the granules, and was shown to crystallize into several single helical crystal structures (V_a, V_h, and E_h-type). The V- and E-type structures are typical of the complexes formed between the amylose and the lipids (i.e., fatty acids) present in cereal starch.[20] Amylopectin which acts as a branched polymer always crystallizes into the B-type crystallinity structure during ageing.[2] E_h-type crystal had not been detected in our research. It was reported that the formation of E_h-type rather than V_h-type structure was favored by low extrusion water content and high extrusion temperature.[21]

The effects of the plasticizing and the glycerol content on the crystal types and crystallinity within 24 h after plasticization are shown in Figure 1. It can be seen that the typical A-type structure has transferred into B- and V-type structure. The typical A-type with the 2θ at 15.0, 18.1, and 22.9° in native starch were all disappeared. The V-type crystals which were mainly caused by the amylose were found in all GTPS immediately after plasticizing with the obvious 2θ at around 7.8, 13.5, 19.4, and 20.8°. The B-type crystal with the 2θ at 22.3 and 26.1° was only found in GTPS30 within 24 h after plasticization. It suggests that the formation of the B-type structure was quicker in GTPS with less glycerol content than that with high glycerol content.

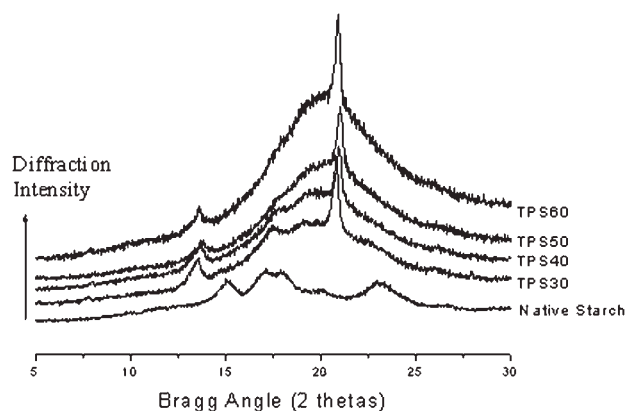There are two sharp peaks with the 2θ at 13.5 and 20.8°. They were classified to be V-type structure.

Figure 1 XRD diffractogram of native starch and GTPS with different glycerol content within 24 h after preparation.

The changes of their height during ageing are listed in Table I. From the data of the same time in Table I, we can see that with the increasing of the glycerol content, the heights of the two peaks increased, which means the V-type structure was easier to be formed in low glycerol content GTPS than that in higher ones. This may have occurred because the mobility of the starch chains increases as the plasticizer content increases and so, the amylose molecules dissociated from the starch granulates would be easier to rearrange during ageing. However, with the increasing of the glycerol content, the percentage of the starch in the ternary system declines, so the small increment of the V-type crystal will not affect the properties of the GTPS much.

Figure 2 shows the changes of the X-ray diffractograms of different GTPS materials during ageing on 0, 7, 21, 54, and 134 days. It seems that the shape of the curves changed a little during ageing, which suggests no significant crystal type changes within 134 days. The little difference is that there were no B-type crystal in GTPS50 and 60 within 24 h after processing, but they appeared immediately in GTPS30 and 40, which also demonstrates the high glycerol content can restrict ageing.

Some researchers have mentioned that the amount of amylose crystals would not change after the initial storage period.[22] Findings in our research will give more information on the change of the amylose crystallinity. We detected that the height of the peaks increased slightly during ageing. From the data in Table I, we can see that in all GTPS, the increase was faster in the first 7 days than that from 7 to 54 days, and the height of these two peaks almost did not change any more after 54 days. This result provides the evidence for the fast crystallization of amylose.

We also noticed that the increment of the two peak's height was closely related to the glycerol content. The increase in GTPS with higher glycerol content was faster than that with lower content. The heights of the two peaks in GTPS50 and GTPS60 were two times higher on 134 days than that on 0 day, but the increase in GTPS30 was only 1.2 times higher on 134 days than that on 0 day, which also indicates that the crystallinity of the amylose was closely correlated with the glycerol content, so the high glycerol content was helpful to the formation of the V-type structure.

In conclusion, the high glycerol content was helpful in the formation of the single helix structure of V-type, but it was limited to the double helix structure of B-type. It was prevalently considered that the reason of ageing is mainly due to the formation of the intermolecular double helix and B-type crystallinity structure.[22–25] The amylose function during ageing is still not very clear. In this work, we find that the crystalline velocity of the amylose is consistent with the ageing velocity reported by Soest et al. that the ageing is quicker in the initiatory times.[26] It illustrates that besides the important effect of the crystallization of amylopectin on ageing, the crystallization of amylose also has some contributions to the ageing. It may be due to that a number of V-type crystals were formed in the initiatory times of the ageing. These small crystals would act as the physical crosslinking points in the material, which can help to change the mechanical properties during ageing.

Thermal behavior

The DMTA was chosen to give information on the changes of thermal properties and the glass transi-

TABLE I
The Height of the Crystal Peaks at $2\theta = 13.5$ and $20.8°$ during Aging

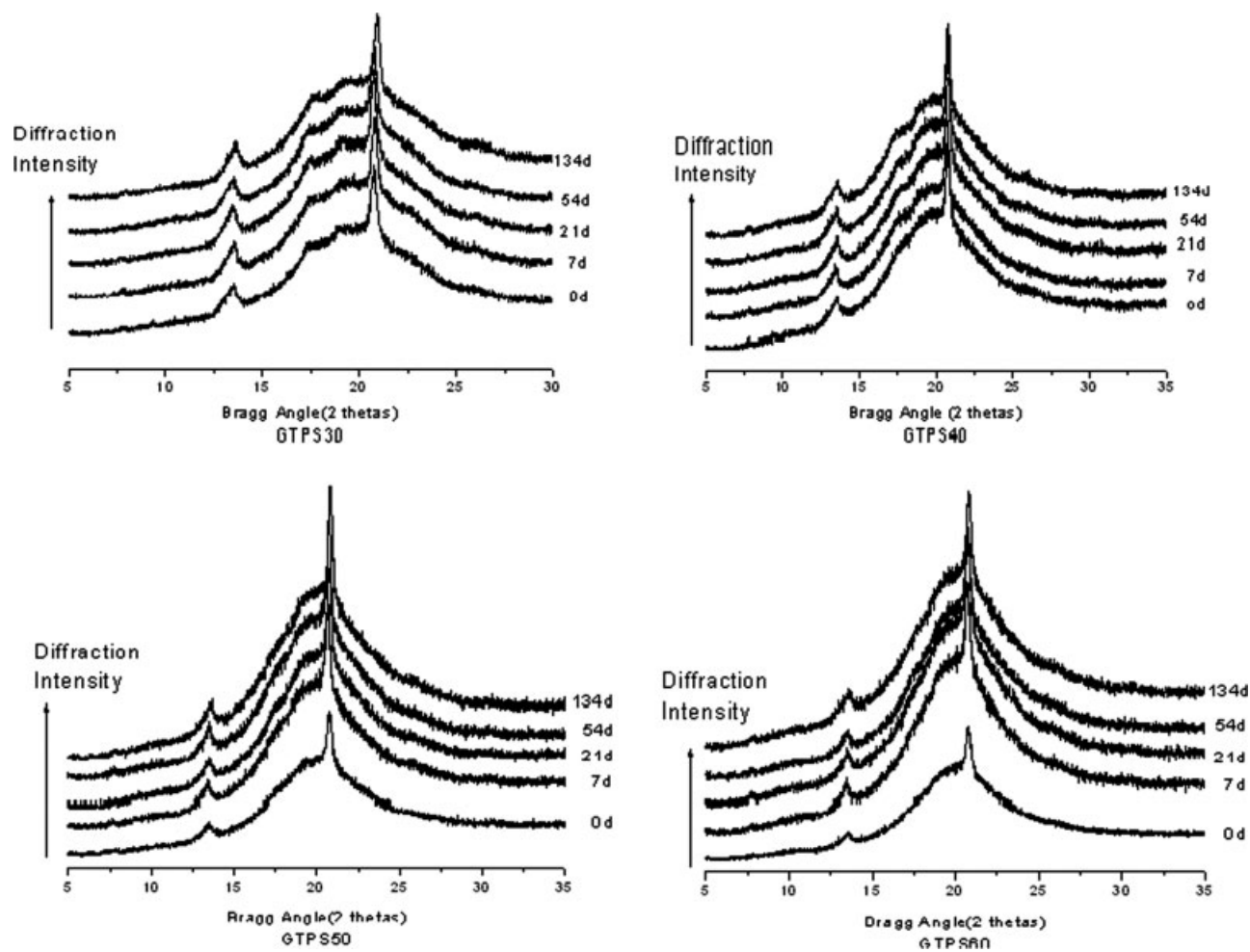|	Sample							
	GTPS30		GTPS40		GTPS50		GTPS60	
Time (d)	13.5°	20.8°	13.5°	20.8°	13.5°	20.8°	13.5°	20.8°
0	1641.2	5189.9	1592.8	6036.0	1572.72	6806.81	2127.8	9690.5
7	1649.7	5556.9	2271.6	7742.8	2304.72	10847.63	4228.6	18085.6
21	1753.1	5863.4	2275.5	8048.1	2339.76	11211.91	4375.0	18220.7
54	1823.1	6075.3	2264.4	8338.9	3050.79	13376.53	4405.0	19194.8
134	1842.4	6066.5	2257.2	8320.1	2907.18	12924.69	4420.0	18327.7

Figure 2 XRD diffractograms of different GTPS materials as a function of time.

tion temperature during ageing. Two main thermal transition regions were observed [See Fig. 3 (A)]. The lower transition is around −60°C, and the other is very wide, nearly from −20 to 145°C, which is called upper transition, thus it is hard to define a single transition temperature, but a glass transition region would be more exact. The onset temperatures of the upper transitions of different GTPS materials during ageing were compared to comprehend the effects of the glycerol content and the storage time. It was reported that the broad upper transition region was caused by a certain extent of heterogeneity in the test material,[27] and the small peaks between −20 and 145°C were considered to be caused by the movements of groups and short chain segments. The upper transition is due to a starch-rich phase, whereas the lower transition is due to a starch-poor phase, which is rich in the glycerol and water content, but still contains a small amount of starch molecules. Two transitions were also detected by DSC (see Fig. 4), which agrees with the result of DMTA. The upper transition on DSC curve is not as obvious as that observed with DMTA, so the DMTA proves to be a more sensitive

tool than DSC which consists of that reported in other works.[28] The existence of two thermal transitions indicate that the phase separation, which is very common in highly plasticized GTPS does exist in the system. Although the glycerol content was high enough for the phase separation to take place, we did not discover the glycerol exudation on the surface of the samples which were stored for a long time. To detect the glycerol content in the samples, the glycerol in the GTPS which was stored for 3 months was removed by immersing the sample bars in the pure water. After 3 days immersion, samples were taken out and subsequently freeze dried until they are completely dry, then weighted. The initial dry weight and wet weight are W_1 and W_0 respect, and the dry weight after immersion is W_2, so the $[(W_1 - W_2)/W_0]$ stands for the glycerol content in the material. We chose the GTPS40 and GTPS60 for the detection, and the glycerol contents in them were 46.24 and 55.04%, which was similar with the initial content. The result demonstrates that no obvious glycerol's exudation happen even when the content reached to 60% after 3 months storage, which may be caused by the strong hydrogen
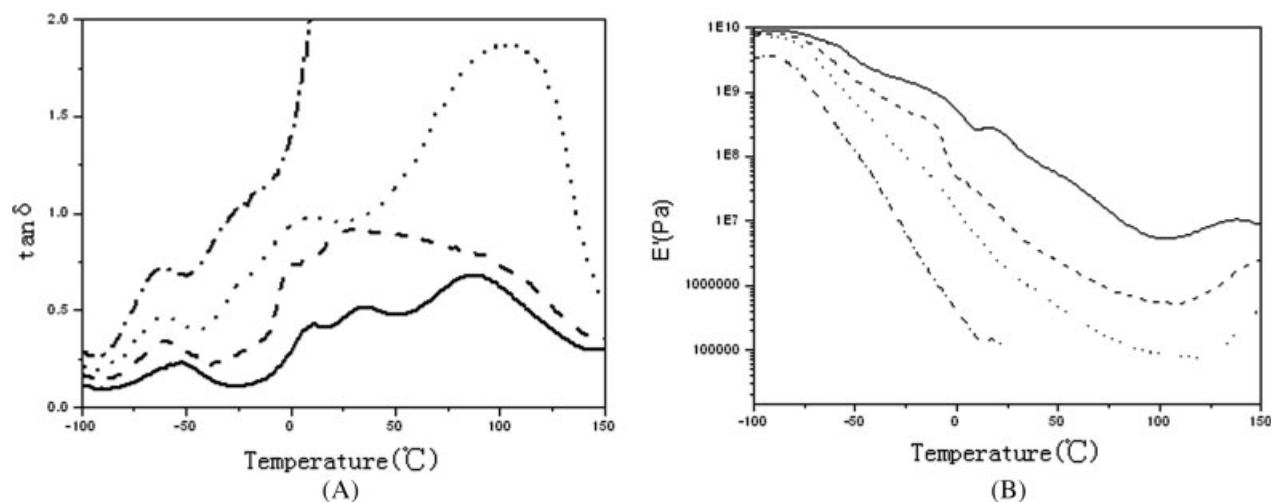
Figure 3 Temperature dependence of the tan δ and storage modulus (E') measured at 10 Hz for the different GTPS materials: (—) GTPS30; (– – –) GTPS40; (· · ·) GTPS50; (– · –) GTPS60.

bonding between the starch and the glycerol Furthermore, abundant water in material also played an important role to fix the glycerol because of its strong hygroscopic property. The exudation also has significant relationship with the humidity. When the environment humidity is low enough, the water inside the material will diffuse into the environment, which result in the exudation of the glycerol. When the ambient humidity is high, the TPS will absorb the water from the environment, and thus the glycerol exudation will hardly happen.[29]

Figure 3(A) also shows the variation of the dissipation factor tan δ and storage modulus (E') in different GTPS materials. The GTPS60 was so weak that the sample broke when the temperature went up to 10°C. The tan δ went up as the glycerol content increased [Fig. 3 (A)]. The storage modulus (E')

dropped as the glycerol content increased [Fig. 3 (B)]. We also noticed that both the peak temperature of the lower transition and the onset temperature of the upper transition went down with the increase of the plasticizers content. It may be caused by the increment of the mobility of starch chains when the glycerol content increased. When the glycerol content was more than 40%, only a slight decrease of the lower transition temperature happened even when the glycerol increased from 40 to 60 wt %. When the transition temperature decreased to the freezing point of the mixture composed with glycerol and water, it would not change any more.

Another interesting phenomena is that in all GTPS, the E' rose when the temperature is above 100°C [see Fig. 3 (B)]. Early research work suggested that it was caused by the water lost[30] and in order
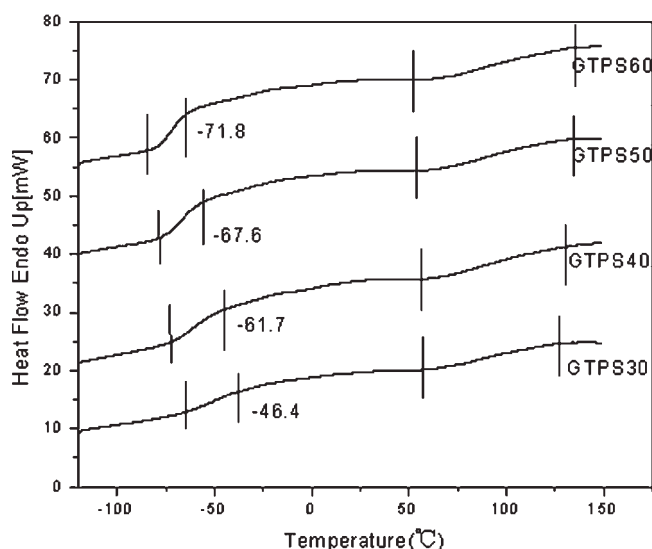

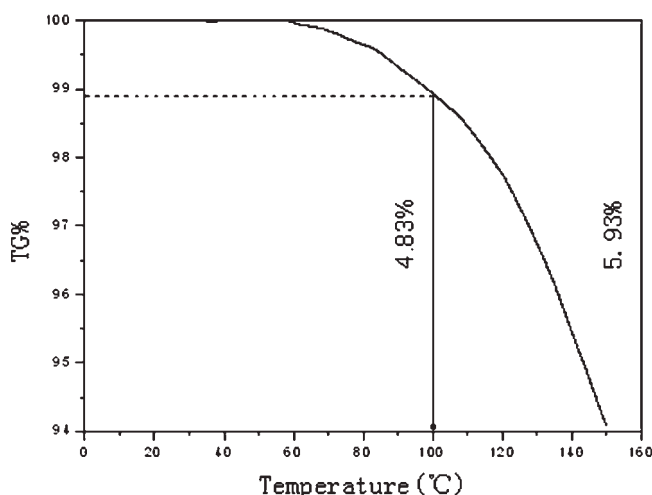**Figure 4** The heating DSC traces of different GTPS materials.

Figure 5 The weight lost of GTPS40 when the temperature increasing from room temperature to 150°C at the speed of 3°C/min.
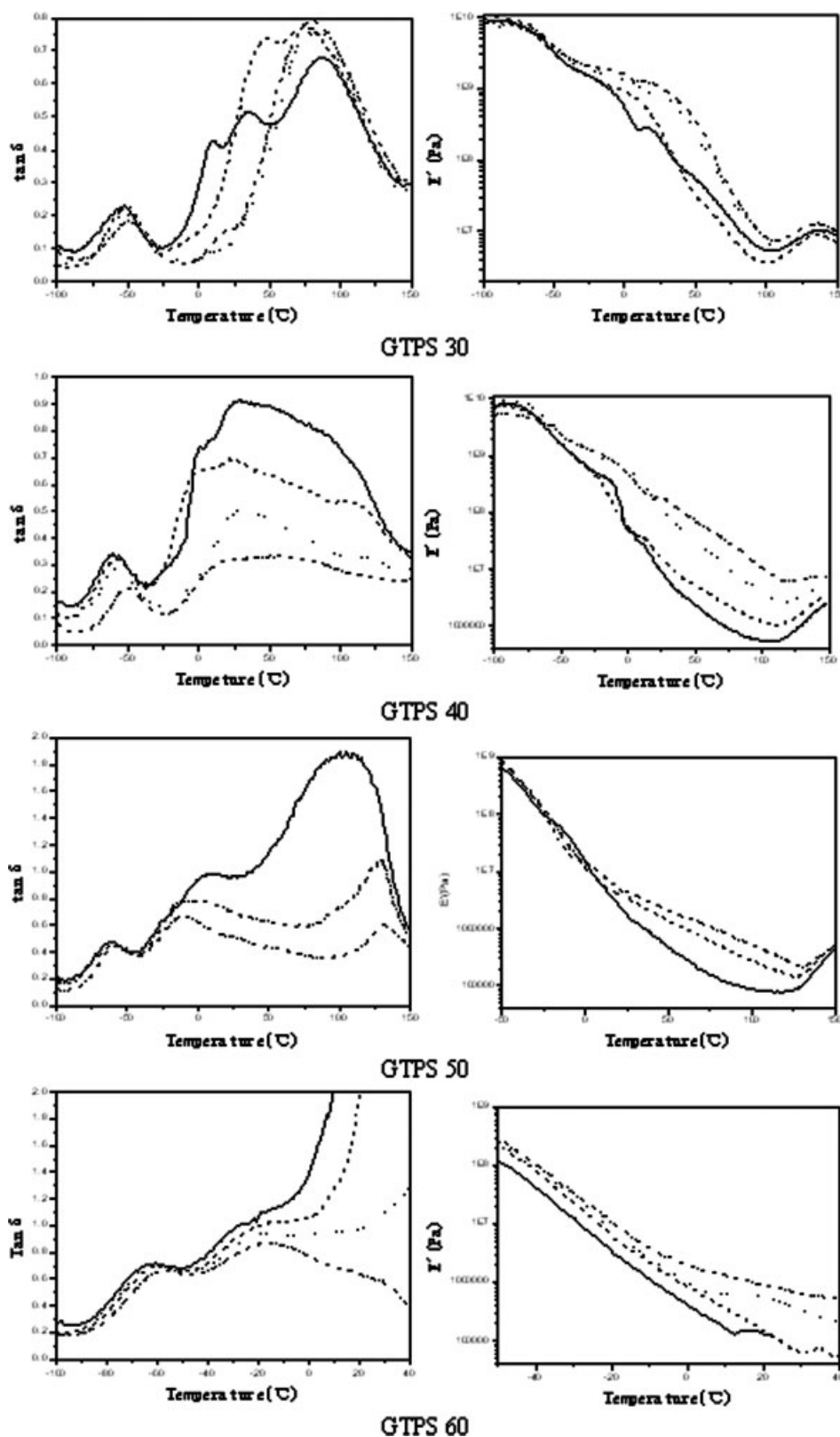
Figure 6 The changes of the tan δ and storage modulus (E′) with plasticizers content depending on time: storage time: 0, 7, 21, and 54 days.

to confirm this, the thermo gravimetric (TG) analysis was used. The temperature range was from room temperature to 150°C with the same heating speed as that

used in DMTA to test the water lost during heating. Figure 5 shows that the total weight loss in the heating processing is 5.93%, in which 4.83% was lost above

TABLE II
The Transition Temperatures and the Heights of tan δ of the Lower Transition Peaks

	Samples							
	GTPS30		GTPS40		GTPS50		GTPS60	
Time (d)	Temp (°C)	tan δ	Temp (°C)	tan δ	Temp (°C)	tan δ	Temp (°C)	tan δ
0	−52.9	0.25	−60.0	0.34	−62.9	0.48	−62.9	0.71
7	−52.8	0.22	−58.0	0.32	−	−	−61.9	0.69
20	−50.1	0.18	−54.9	0.29	−59.0	0.47	−60.7	0.72
54	−50.0	0.17	−52.1	0.21	−56.8	0.44	−56.9	0.68

100°C. The onset temperature for the heat decomposition of the starch molecules is above 150°C, and the glycerol's boiling point is 290°C. So the weight lost was mainly caused by the water evaporation. The dramatic change of the E' value at only 5.93% water loss reflected that the GTPS material is very sensitive to water as that reported in other work.[31]

Figure 6 shows the change of the tan δ and E' of different GTPS materials during ageing (from 0 to 54 days). The temperatures and values of the lower transition peaks during ageing were given in Table II while the onset temperatures (the point from which the peak of the tan δ start to go up) of the upper transition were displayed in Table III. Results show that with the time passing by, both the peak temperatures of lower transition and the onset temperatures of the upper transition increased as well as the E' modules, opposite of the tan δ. The number of the peaks was also declined in the upper transition region during ageing, which is more obvious in the GTPS30 and GTPS40. This is caused by the relaxation of the shear-induced orientation of the starch chains during ageing. The system was translating into a more equilibrium state.

The changes of the transition temperatures and the value of the tan δ may be due to the recrystallization. During ageing, the starch chains which have been separated by the plasticizers will connect again. The B-type crystal structure was formed gradually. Formation of the B-type structure was thought to be the main reason for retrogradation.[22] The V-type structure which was induced by the amylase was also formed right after the process. The small crystal regions that are formed during ageing will act as the physical crosslinking points which will limit the movement of the starch chains, so the relative slide movement between molecules was restrained, which results in the decrease of the tan δ and increase of the E'. With the time passing by, more and more small crystal regions were formed to limit the movements of the starch molecules, so the higher temperatures will be required for the chain segments to move. As a result, the T_g increases gradually during ageing. The results are consisted with that obtained from the low glycerol content GTPS, but the increased speed was slowed down by the high amount of glycerol which can separate the starch molecules.

The increase of the lower transition temperature can be explained by assuming that the starch poor phase is a solution in which a small number of starch molecules act as the solute and the mixture of water and glycerol make up the solvent. With the time passing by, more and more starch molecules dissolved in the solvent, inducing the increase of the lower transition temperature.

To illustrate that the high glycerol content can restrict ageing, the onset temperatures of the upper transitions of different GTPS materials were compared in Table III, which was never reported in any other work. From 0 to 54 days, the increase of the onset temperature of GTPS30 was 15°C while the increase of GTPS60 was only 5°C, which means the increase of the T_g of GTPS30 was much quicker than that of GTPS60. It could also be a good evidence to illustrate that the high glycerol content is helpful for preventing ageing. We also noticed that the increase of the temperature was much quicker in the first 7 days than that after 7 days when the glycerol content was not high enough (GTPS30 and GTPS40). The results agree well with the finding of van Soest et al., who proposed that the ageing velocity is quick at the initiatory times.[26] However, when the glycerol content was high enough (see GTPS50 and GTPS60), the increase of the onset temperature of higher transition during ageing was slower than that with lower glycerol contents.

Mechanical properties

Typical stress-strain curves of different GTPS materials are shown in Figure 7. The materials with lower glycerol content (like GTPS30) were tough with rela-

TABLE III
The Onset Temperatures (°C) of the Upper Transition Dependent on the Plasticizers Content and the Aging Time

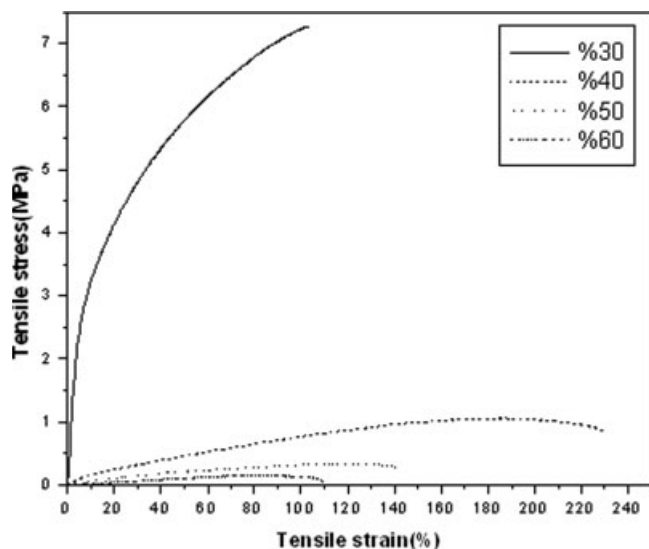|	Samples			
Time (d)	GTPS30	GTPS40	GTPS50	GTPS60
0	−26.99	−37.79	−45.09	−50.05
7	−21.95	−34.97	−	−50.00
21	−18.89	−27.69	−45.97	−48.78
54	−12.03	−25.05	−44.76	−45.07

Figure 7 The stress-strain curves dependent on the glycerol content.

tive high E modulus (23.0 MPa) and small elongation at break (115.3%), which behaved more like the ordinary plastic. With the increase of the glycerol content (see GTPS40), the E modulus decreased and

the elongation at break increased. The E modulus of GTPS40 was about 1.7 MPa and the elongation at break increased to 204% within 24h after processing, so more elastomeric properties were presented than GTPS30. We also noticed that when the glycerol content is above 50%, the E modulus and the elongation at break all decreased as the glycerol content increased, which may be caused by the destruction of the interactions among the starch molecules. The material became so weak that it can be broken easily. The E modulus and the elongation at break of GTPS60 right after processing course were only 0.3 MPa and 170%, which behaved like a silicon rubber.

The stress-strain curves of different GTPS materials during ageing were shown in Figure 8. The GTPS60 was so weak that the stress-strain curves of it were influenced by the vibration of the environment. The E modulus and the tensile strength increased and the elongation decreased with the time passing by (see Fig. 8 and Table IV). The changes of GTPS30 were more drastic than that of other GTPS materials. The number of cracks in the tensile bars increases in time with the increase of crystallinity, so the sample bars of GTPS30 that conditioned at RH 50% and 37°C for more than 40 days
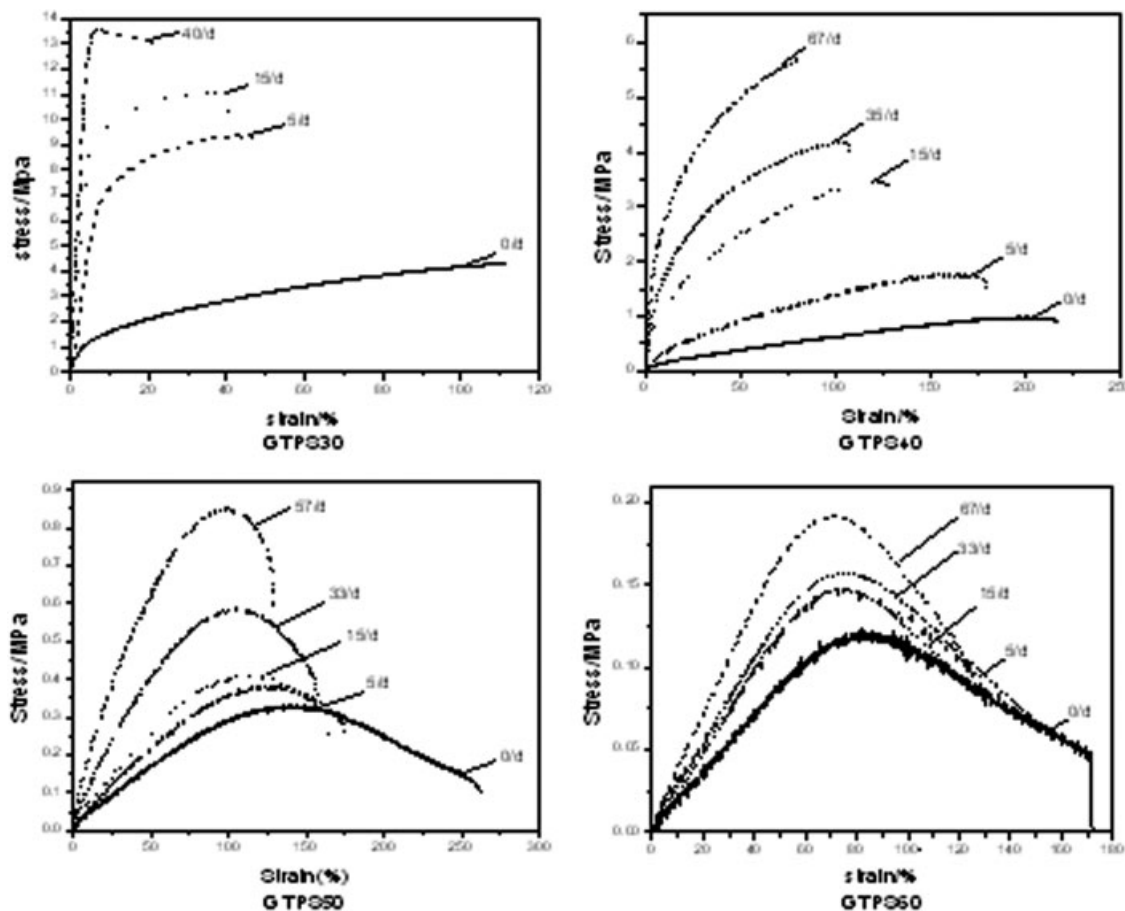

Figure 8 The stress-strain curves as a function of time.

TABLE IV
The Elongation at Break (%), Permanent Set (%), and the Shore A Hardness (°)
of Different GTPS Materials Dependent on Time

Time (d)	Elongation at break (%)				Permanent set (%)				Shore A hardness (°)			
	GTPS30	GTPS40	GTPS50	GTPS60	GTPS30	GTPS40	GTPS50	GTPS60	GTPS30	GTPS40	GTPS50	GTPS60
0	115.3	204.3	245.3	170.2	13.1	15.8	46.7	30.0	89.1	75.1	55.2	34.4
5	55.2	166.3	205.5	168.3	12.7	8.8	25.7	15.0	90.2	87.2	55.5	34.1
10	42.3	145.7	195.8	153.1	9.1	10.2	26.7	13.3	93.0	89.1	56.0	34.3
15	38.8	130.4	175.0	143.6	7.1	6.7	14.9	11.0	93.5	93.0	58.1	35.2
25	15.2	115.5	173.9	120.2	5.2	6.1	15.1	10.9	94.0	93.1	60.3	37.1
35	6.4	95.0	158.0	120.1	4.4	5.2	13.9	11.1	98.2	96.0	68.2	63.1
67	–	73.5	134.2	120.4	–	5.5	12.4	11.6	–	98.0	72.1	48.2

showed a very brittle behavior, so the mechanical testing was impossible to be done after 40 days. However, the GTPS50 and GTPS60 just had very slight changes in 67 days. This result strongly supports the original hypothesis that is obtained from the XRD and DMTA, which is that the high glycerol content does have the effect to restrain ageing and the retrogradation rate is quicker at the beginning than at the end. The permanent set and the shore A hardness of different GTPS materials during ageing were also detected and listed in Table IV. It can be seen that the permanent set of different GTPS materials all decreased, while the shore A hardness increased with the time passing by.

From the results of mechanical test as well as the results obtained from the XRD and DMTA, we suppose that the change in crystallinity effected the stress-strain behavior much of the GTPS materials. It can be explained by assuming that the thermoplastic starch consists of a molecular network of semicrystalline amylose and amylopectin with some granular segments (composed of residual swollen granules, partially melted, deformed, and disrupted granules as well as the recrystallized starch). With the time passing by, an increase in the number of the crystal regions composing acted as the physical crosslinking points which results a reinforced network,[22] and so the *E* modulus and the hardness increased. At the same time, the elongation between the points was restricted, which results in the decrease of the elongation at break.

FTIR spectra

Infrared spectroscopy has been used for investigating changes in starch structure on a short-range molecular level. The hydroxyl groups in glycerol destroy the original hydrogen bonds between starch molecules and make it thermoplastic. The FTIR is an effective tool to estimate the influence of the glycerol content and the ageing time on the hydrogen bonds in GTPS materials

The effect of the plasticizing and the glycerol content on the IR bands are shown in Figure 9. The peak of hydroxyl group stretching in native starch is at 3413 cm^{-1}. The height of this peak was lower in GTPS than that in native starch. It seems that the wavenumbers of the hydroxyl group-stretching peak
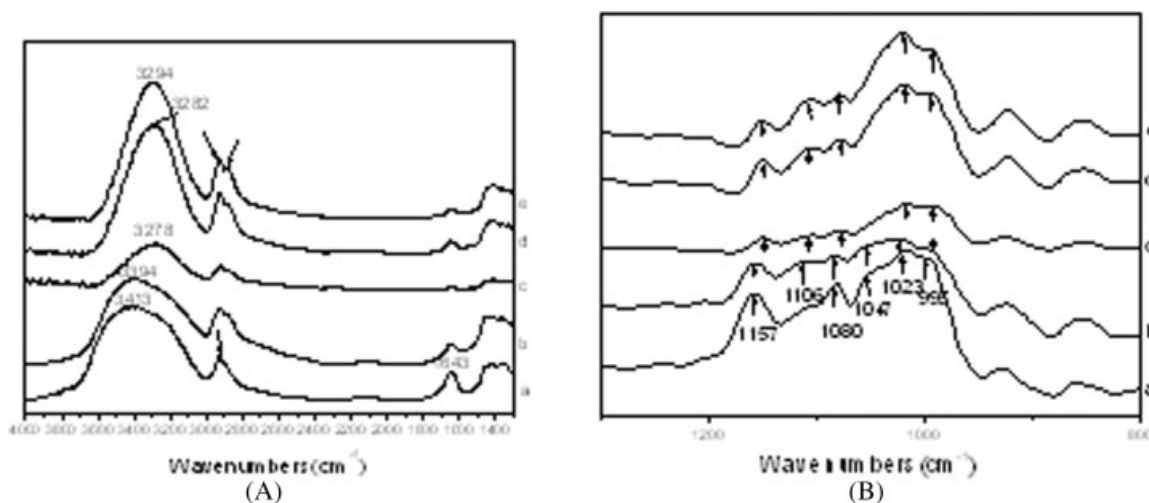

Figure 9 FTIR spectra of the native starch and the different GTPS materials: (a) native starch; (b) GTPS30; (c) GTPS40; (d) GTPS50; (e) GTPS60.
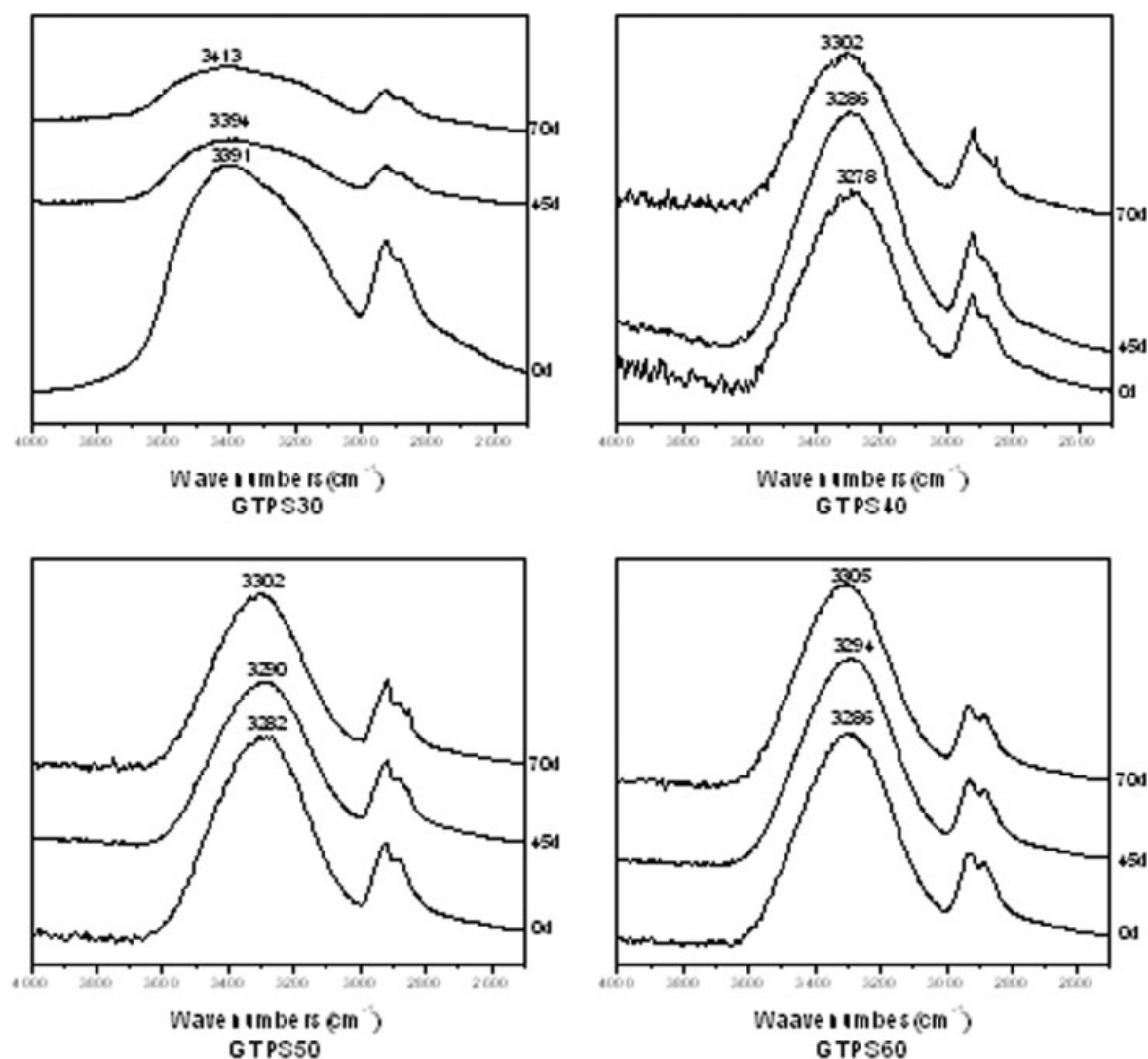
Figure 10 FTIR spectra of different GTPS materials dependent on time.

declined and the height of the peak increased as the glycerol content increased. This may have occurred because the number of the hydrogen bonds increased with the increase of the glycerol. When the glycerol content increased, more and more plasticizers molecules assembled together, which enhanced the interaction between the hydroxyl groups.

The peak around 2920 cm^{-1} is characteristic of the H—C stretching, and the shape of it changed slightly from the single peak in native starch to a double-peak in GTPS as seen in b, c, d, and e [Fig. 9(A)], which was caused by the different stretching of the H—C on the starch molecules and on the glycerol molecules. There are several characteristic peaks on the IR absorbance band of native starch. The 1150, 1124, and 1103 cm^{-1} are corresponding to the C—O, C—C stretching with some COH contributions, while 1077, 1047, 1022, 994, and 928 cm^{-1} is corresponding to the COH bending and CH$_2$ related modes.[32,33] It was reported that the band at 1047

cm^{-1} is sensitive to the amount of ordered or crystalline starch and the band at 1022 cm^{-1} is characteristic of amorphous starch. The ratios of the bands at 1047 and 1022 cm^{-1} could express the amount of ordered starch. The band at 994 cm^{-1}, which is related to the intramolecular hydrogen bonding of the hydroxyl at C$_6$, is water sensitive.[34]

It seems that the less of the glycerol content, the higher of the peak at 1047 cm^{-1}. We can see that the peak at 1047 cm^{-1} in GTPS30 [Fig. 9(B) b] was still obvious when compared with that in native starch [Fig. 9(B) a], but with the glycerol content increasing, the shoulder at 1047 cm^{-1} disappeared, as shown in Figure 9(B) c, d, and e, which demonstrates again that the crystallinity decreased as the glycerol content increased. On the contrary, the peak at 995 cm^{-1} became more and more obvious with the increasing of glycerol content [Fig. 9(B)], which indicates that the sensitivity to water increased as the glycerol content increased.
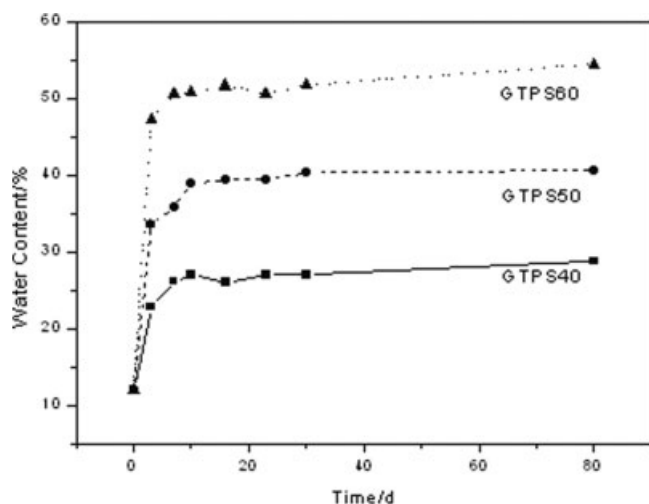
Figure 11 Water content (%) as a function of storage time for GTPSs under 37°C and RH, 50%.

The peak at 1106 cm^{-1} was more obvious in GTPS materials than that in native starch, which suggests the microenvironment around the O—C groups was changed when the glycerol was added, and a molecular lever interaction between the starch and the glycerol appeared.

The variation of the hydroxyl group-stretching peaks during ageing is shown in Figure 10. The shifting and broadening of hydroxyl group stretching bands were observed, which indicated that there was a specific change of hydrogen bonding between the starch chains and the plasticizers. The peaks were shifting to higher wavenumber in all GTPS materials during ageing. The tendency was to approach the state in native starch, whose peak of hydroxyl group stretching is at 3413 cm^{-1}. We noticed that after 70 days, the peak of GTPS30 was at 3413 cm^{-1}, which was as same as that in native starch. The shifting of the peak can be explained by assuming that the interaction between the plasticizers and the starch molecules is gradually reduced. With the time passing by, the plasticizers was getting together, as a result the phase separation happened and became more and more obvious, which was also reflected from the peak of 3413 cm^{-1}. It can be seen that longer the storage time, the wider this peak. That is because the O—H stretching in the liquid phase was moving to the lower wavenumbers, while the O—H stretching in the crystalline phase was transferring to the higher wavenumbers during ageing, which results in the increment of the width of the peak. This finding not only well supports that the phase separation existed, which we have obtained from DMTA, but also suggests the phase separation became more and more obvious during ageing. The result also shows that the shifting speed fell as the glycerol content increased. The results from

FTIR demonstrate again that the high glycerol content can restrain ageing, which is well consistent with that we have obtained from the analysis of the XRD, DMTA, and mechanical properties.

Water absorption

As shown in Figure 11, the water absorption of GTPS increased as the glycerol content increased, which is due to the great water hygroscopic property of the glycerol. For all GTPS materials, the water absorption speed was very quick in the first 7 days. From the results of XRD, DMTA, and mechanical measurements, the changes of the crystallization and mechanical properties was much faster in the initiatory times than that in the latter days of the ageing, so we can deduce that was partially caused by the dramatic increase of the water content in the initiatory time of the ageing. Although increased water content by increased glycerol content, ageing speed of the high glycerol content GTPS was still slower than that of the low content GTPS, which demonstrates well that glycerol can resistant ageing.

After 7 days, there was only a slight change of the water content and finally, the GTPS reached to an equilibrium state. So from 7 to 80 days, the influence of the water content on the crystallization and mechanical properties could be neglected.

CONCLUSIONS

A kind of soft and better ageing resistant thermoplastic starch was prepared by melt blending with high glycerol content. A series of studies have been done on the ageing of the thermoplastic corn starch with the high glycerol content under a normal human body temperature (37°C) and a comfortable relative humidity for human being (RH 50 ± 5%). Result of XRD suggests that high glycerol content is helpful to the formation of the single helix structure, but it limits that of double helix structure of B-type. DMTA measurement showed that the onset temperature of the upper transition of the GTPS with less glycerol content increased more quickly than that with high glycerol content. The stress-strain measurement presented a slow changing when the glycerol content was over 40 wt %. Result of FTIR shows that the shifting speed of the peak of hydroxyl group stretching decreased as the glycerol content increased. FTIR also suggests that the phase separation not only existed, but also became more and more obvious in the GTPSs. The results from all characterizations demonstrate that the high glycerol content can prevent ageing effectively. The usage of plasticizers with other polar groups, which have stronger interaction with the starch molecular than glycerol, may be another way to restrain ageing. Furthermore,

big molecular plasticizers may serve more stable to separate the starch molecules than the small molecular plasticizers do. The influences of other plasticizers are to be considered in further research.

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