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Influence of oxidized starch on the properties of thermoplastic starch

Yu-Rong Zhang, Xiu-Li Wang*, Guo-Ming Zhao, Yu-Zhong Wang*

Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, National Engineering Laboratory of Eco-Friendly Polymeric Materials, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610064, China

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ABSTRACT

Thermoplastic starch was prepared by adding oxidized starches and glycerol together into starch. The addition of oxidized starch improved the rheological properties and also increased the toughness of thermoplastic starch. Compared with TPS30, the elongation at break increased from 126.8% to 152.5% when 5 wt% OS 117% was added. Good compatibility of thermoplastic starch between the matrix and oxidized starch was confirmed by SEM. The addition of oxidized starch lowered the storage modulus and glass transition temperature (T_g) of thermoplastic starch, decreasing T_g from 34.1 to 30 °C when 10 wt% OS117% was added. The thermal stability of blending was improved by adding oxidized starches, i.e. when 5 wt% OS70% was added, $T_{5\%}$ increased from 134 to 156 °C.

1. Introduction

Recently, the bulk production of biodegradable materials has been the subject of intense investigation in both industries and academia, because of the growing shortage of petroleum resources and the inherent non-biodegradability of petroleum-based materials (Zhang et al., 2013). Starch, which is produced by many green plants as an energy store, has been considered as an attractive and optimum candidate to replace the petroleum-based materials. Major advantages of starch include its inherent biodegradability, ubiquitous availability, relatively low cost (Teixeira, Dá Róz, Carvalho, & Curvelo, 2007) and the ease for chemical modifications (Labet, Thielemans, & Dufresne, 2007; Sung, Park, Park, Choi, & Jhon, 2005).

The preparation of thermoplastics from starch has been investigated during the past few decades. In fact, starch is different from other synthetic polymers. It cannot be considered as truly thermoplastic, because its glass–rubber transition temperature (T_g) is higher than its decomposition temperature when it has been dried. By using conventional processing techniques, such as extrusion, internal mixing and injection molding, which is usually used in the processing of typical synthetic thermoplastics, native granular starch can be converted into a molten state in the presence of plasticizers, such as water and/or glycerol (Xie, Halley, & Avérous, 2012). In general, the addition of plasticizers into starch is an established method for lowering the T_g of starch below its decomposition temperature (Mathew & Dufresne, 2002a) and converting starch into a so-called thermoplastic starch, which can be processed easily (Averous, Fringant, & Moro, 2001; Huneault & Li, 2007; Sarazin, Li, Orts, & Favis, 2008).

Plasticizers are usually low molecular weight substances, which make them easier to incorporate into the polymer matrix to destroy the inter- and intra-molecular hydrogen bonds that occur in starch, and thereby increase the free volume between molecular chains and molecular mobility of polymers. As a result, the toughness and thermal processing conditions of starch-based materials are improved compared to native starch (Mathew & Dufresne, 2002b; Talja, Peura, Serimaa, & Jouppila, 2008). Glycerol and water are most widely used plasticizers to prepare thermoplastic starch (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006). Higher moisture content can potentially reduce the stiffness of compression-molded starch and increases their ultimate elongation at break, because of the decrease in T_g (Thunwall, Boldizar, & Rigdahl, 2006). Other low molecular weight substances, such as polyols (Mathew & Dufresne, 2002b), citric acid (Yu, Wang, & Ma, 2005), formamide (Wang, Yu, Chang, & Ma, 2008), and urea have also been utilized as plasticizers of starch. The plasticizing effect of different polyols, such as glycerol, xylitol, sorbitol, and maltitol on waxy maize starch was investigated by Mathew and Dufresne (Mathew & Dufresne, 2002b). And it was found that as the molecular weight of plasticizer increased, both stiffness and toughness of the moist material were improved. Furthermore, chemicals containing nitrogen, such as urea and ammonium derivatives (Wang et al., 2008; Ma, Yu, & Feng, 2004), are also effective plasticizers for preparing thermoplastic starch. However, these plasticizers containing amide functional groups are potentially harmful (Yu et al., 2005). Citric acid, which contains three carboxylic acid groups and one hydroxyl group, has

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* Corresponding authors. Tel.: +86 28 85410259; fax: +86 28 85410259.
E-mail addresses: xiuliwang1@163.com (X.-L. Wang), yzwang@scu.edu.cn (Y.-Z. Wang).

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stronger hydrogen bonding interactions with starch as compared to glycerol (Yu et al., 2005). However, starch macromolecules will be depolymerized during processing when citric acid is added (Xie et al., 2012). Moreover, plasticizers which have small molecular weight, can easily penetrate into starch matrix, but they are also easy to migrate out of the matrix during the subsequent processing steps.

Compared with citric acid, oxidized starch with high degree of oxidation also contains many carboxylic acid groups, which can potentially form intra-molecular hydrogen bonds with starch. Due to its macromolecular structure, its migration can be avoided during and after processing. Besides this, unlike citric acid, its introduction will not make starch acid hydrolysis. Therefore, in the present work, oxidized starches with high degree of oxidation were prepared, and then added with glycerol into starch to prepare thermoplastic starch. It was expected that oxidized starch could improve the rheological properties and the toughness of starch. The compatibility between oxidized starch and starch matrix was examined by scanning electron microscopy (SEM). Besides this, the dynamic mechanical properties and thermal stability of thermoplastic starches plasticized by glycerol and oxidized starch were also investigated by DMA and TGA, respectively. To the best of our knowledge, this is the first report using oxidized starch as a macromolecular to improve the properties of thermoplastic starch.

2. Materials and methods

2.1. Materials

Cornstarch (11–13% moisture) was obtained from Langfang Starch Company (technical grade, Langfang, Heibei, China). Hydrogen peroxide (H_2O_2, 30%) and glycerol (analytical grade (99.5%)) were purchased from KeLong Chemical Reagent (Chengdu, China). All chemicals were used as received without further purification.

2.2. Preparation of oxidized starches with different degree of oxidation

The oxidized starch was prepared according to our previous study (Zhang, Wang, Zhao, & Wang, 2012). A typical run was as follows. Starch slurry was prepared by adding starch (dry basic) and 5 (v/w) distilled water into a metal pail. Then the mixture was heated at 80 °C for 30 min with manual stirring to make starch gelatinize adequately. After the temperature was cool below 50 °C, an aqueous $CuSO_4$ (0.01% molar ratio based on glucose units of starch) solution and H_2O_2 (15% molar ratio based on glucose units of starch) were both added drop wise into the starch slurry subsequently. Thorough stirring was followed to make them disperse uniformity. After that, the mixture was placed in an air-forced oven for two days at 50 °C. Then the product was dried 48 h at 60 °C in a vacuum oven and milled into powder. The determination of the degree of oxidation was performed according to our previous method (Zhang et al., 2012). Thus, oxidized starch with 42% degree of oxidation was prepared. In this paper, oxidized starch with 70% and 117% degree of oxidation (abbreviated as OS70% and OS117%) were also prepared with the same method by changing the molar ratio of copper sulfate and hydrogen peroxide.

2.3. Preparation of thermoplastic starch

Thermoplastic starches were prepared by melt extrusion processing using a twin screw extruder. Glycerol and oxidized starches was blended together (3000 rpm, 2 min) with cornstarch in a High Speed Mixer GH-100Y (Beijing, China). Then the mixture was stored 24 h in a plastic bag. After that the mixture was fed into a co-rotating twin-screw extruder (STE 20, Coperion Keya Machinery Co. Ltd, Nanjing, China) at a screw speed of 100 rpm with a temperature gradient along extruder barrel as the following profile: 80 °C, 100 °C, 110 °C, 110 °C, 110 °C, 100 °C (from feed zone to die). Then the extruded strips were cut into particles. In this study, 30 wt% glycerol (based on corn starch) was used for all samples containing oxidized starch. When only glycerol was used as the plasticizer, the thermoplastic starch is abbreviated as TPS30. When oxidized starch was added, the thermoplastic starch is abbreviated as TPS*m*OS*n*, in which *m* stands for the oxidized starch content (weight ratio based on cornstarch) and *n* represents the degree of oxidation. For example, when 5 wt% oxidized starch with 42% degree of oxidation was added into the blending, thermoplastic starch is abbreviated as TPS5OS42%.

2.4. Rheological properties

Thermoplastic starches were cut into small pieces and tested by a capillary rheometer (Rheograph 2002, Gottfert.Co, Germany). After pelletizing and conditioning in 53% relative humidity environment at room temperature for 24 h, the samples were fed into the barrel through a funnel, followed by being preheated for 4 min before being analyzed in the rheometer. The measurements were performed at 100, 110, and 120 °C, respectively. The L/D was 20/1 and the diameter of the die was 2 mm. It has been shown by others that (Onteniente, Abbès, & Safa, 2000) for most thermoplastics, the following power law is used extensively to describe the flow properties of non-Newtonian liquids in theoretical analysis as well as in practical engineering applications (Wang et al., 2008)

$$\tau = K\gamma_a^n \tag{1}$$

The apparent viscosity η (Pa s) is defined by Eq. (2):

$$\eta = \frac{\tau}{\gamma_a} \tag{2}$$

In the above equations K is the consistency, τ is the shear stress (Pa), γ_a is the shear rate (s^{-1}), and n is the index in the power law.

Substituting Eq. (1) into the Newtonian relationship between τ and γ_a (Eq. (2)) yields the following expression, by which viscosity (η) and (γ_a) values can be obtained:

$$\eta = k\gamma_a^{n-1} \tag{3}$$

$$lg\eta = lg\,K + (n-1)lg\gamma_a \tag{4}$$

2.5. Mechanical testing

Compression molding was used to produce sheets/films with a thickness in the range of 0.5–1 mm. All the samples were placed in an environment with 53% relative humidity for one day before the test was performed. The Materials Testing Machine (SANS CMT4104, Shengzhen SANS, China) was run at a crosshead speed of 10 mm/min was used for tensile testing (ISO 1184-1995 standard). The data was the average of 5–8 specimens in each treatment. Tensile strength, elongation-at-break, and Young's modulus were directly obtained from this test.

2.6. Scanning electron microscopy (SEM)

The fractured surfaces of TPS30 and TPSOS were examined using scanning electron microscopy (Philips FEI INSPECT F instrument, FEI, Netherlands) operated at 10 kV. The samples were fractured after immersion in liquid nitrogen, and the surfaces were coated with a thin gold layer before observation.

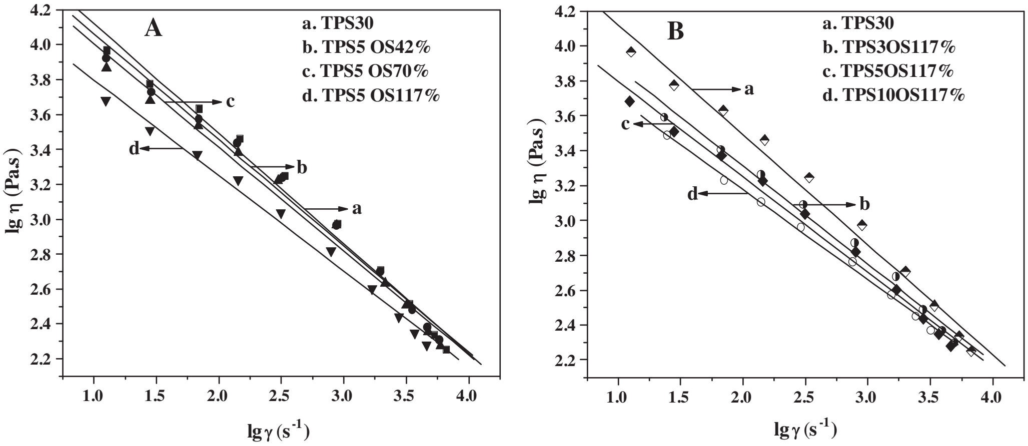

Fig. 1. Rheological curves of thermoplastic starch at 110 °C. (A) Thermoplastic starch containing oxidized starch with different oxidization degree. (B) Thermoplastic starch containing different content OS117%.

2.7. Dynamic mechanical thermal analysis

Thermomechanical properties of the sheets were tested with a dynamic mechanical analyzer (DMA Q800, TA Instruments, U.S.A.). All samples were left in 50% relative humidity environment at room temperature for 24 h before test. Tests were performed using a temperature gradient from −80 to 100 °C with a heating rate of 3 °C/min at an oscillation frequency of 1 Hz.

2.8. Thermogravimetric testing (TG)

Thermogravimetric analysis (TGA) of samples (4–5 mg) was carried out by using a NETZSCH thermal analyzer (TG209F1, NETZSCH (Gerätebau GmbH, Selb/Bavaria, Germany) under nitrogen atmosphere at a heating rate of 10 °C/min. The samples were kept in a vacuum oven at 60 °C for 48 h before test. The range of scanning temperature was from 40 to 500 °C.

3. Results and discussion

3.1. Rheological properties of thermoplastic starch

During the processing and testing process, water was absorbed inevitably by thermoplastic starch. The moisture absorptions of thermoplastic starch containing oxidized starch are tested at RH 53% and RH 100% condition, respectively (shown in supplemental materials). It was found the addition of oxidized starch almost had no effect on the moisture absorption, no matter the variation of the degree of oxidation or the weight ratio of oxidized starch (Fig. 1S). The final moisture absorption of TPS5OS42%, TPS5OS70%, and TPS5OS117% are 7.6%, 7.6% and 7.7%, respectively, which are almost same as that of TPS30. The similar results are also obtained for samples conditioned in RH 100% (Fig. 1Sb). Therefore, the effect of moisture absorption on the properties can be excluded here.

The apparent viscosities of thermoplastic starch were determined as a function of the shear rate. The η–γ_a curves were plotted using a double logarithmic chart. Fig. 1 shows the effect of the degree of oxidization (Fig. 1A) and the content (Fig. 1B) of oxidized starch on the rheological properties of thermoplastic starches. Upon increasing the shear rate, the viscosity of all thermoplastic starches samples decrease correspondingly, which indicates that the melts of the extruded starch blends behave like a pseudoplastic fluid. With the increase of shear rate, the entanglement of starch chains decreases, which leads to the gradual weakening of the inter- and intra-molecular interactions between starch and therefore reduced the flowing resistance (Wang et al., 2008). Hence, a highly disperse and compatible blend can be achieved by increasing the shear rate to obtain a lower viscosity. As shown in Fig. 1A, oxidized starch with different degrees of oxidation has a great effect on the rheological behavior of thermoplastic starches. With the increasing degree of oxidation, while holding all of the other parameters constant, the apparent viscosities of the blends decrease correspondingly. We found that the carbonyl group mainly exists as carboxylic group when its content exceeds 39% in our previous study (Zhang, Zhang, Wang, Chen, & Wang, 2009). Carboxylic acid groups can establish strong hydrogen bonds with starch and partially replace the interaction of hydrogen bonds between different starch chains. When materials are performed at low shear rate, the effects of oxidized starches on the rheological properties are more obvious (Fig. 1A). When the shear rate increases, the extruded starch blend undergoes shear thinning and decreases the effect of oxidized starch on the apparent viscosity.

From Fig. 1A, it appears that OS117% leads to a greater depression in starch's apparent viscosity. Therefore, the effect of OS117% contents on the rheological properties of thermoplastic starch was investigated and the results are shown in Fig. 1 B. It appears that increasing OS117% content significantly decreases the melting viscosity, due to a higher amount of carbonyl groups, which can form hydrogen bonds with the hydroxyl groups of starch molecules, and further results in the disruption of inter- and intra-molecular hydrogen bonds of starch.

3.2. The effect of oxidized starch on non-Newtonian index

Non-Newtonian index n estimates the extent of deviation of polymer liquid from Newtonian liquid. As the n value approaches 1, it behaves like a Newtonian fluid, which means that it is less sensitive to shear rate. Non-Newtonian index n is influenced by numerous factors such as temperature, shear rate, molecular weight, configuration of polymer, plasticizer type and content, and interaction between molecular chains and so on. According to Eq. (4), in the double logarithmic curves of shear rate versus apparent viscosity (Fig. 1), the slope of the linear fit equation is $n-1$ and the intercept is $\lg K$. The data is well fit to the simple power law model (Eq. (3)) with high determination coefficients ($r_2 = 0.992$–0.995), as shown in Table 1. All samples possess high shear thinning behavior, flow behavior indices (n) are in the range of 0.37–0.48. An n value lower than 1 indicates that the molten thermoplastic starches shows shear thinning behavior, which is mainly ascribed to the gradual reduction of molecular entanglement with the increase of shear rate (Xie et al., 2012). The magnitude of the consistency index (K) obtained from the power law model decreases from $10^{4.67}$ to

Table 1
The influence of OS on the non-Newtonian index *n* of TPS.

Samples	Non-Newtonian index *n*	*R*	*K*
TPS30	0.37 ± 0.03	0.993	$10^{4.75\pm0.07}$
TPS5OS42%	0.39 ± 0.03	0.993	$10^{4.67\pm0.07}$
TPS5OS70%	0.41 ± 0.03	0.992	$10^{4.60\pm0.07}$
TPS3OS117%	0.44 ± 0.02	0.985	$10^{4.44\pm0.07}$
TPS5OS117%	0.45 ± 0.02	0.995	$10^{4.35\pm0.05}$
TPS10OS117%	0.48 ± 0.01	0.998	$10^{4.21\pm0.03}$

$10^{4.35}$ with increasing the degree of oxidation from 42% to 117%. The Non-Newtonian index *n* increases with increasing degree of oxidation, which indicates that the samples become more like Newtonian liquid, and therefore the rheological properties of thermoplastic starch are improved. When conventional plasticizers and starch are blended together, the hydrogen bonds between these two are established (Ma et al., 2004), which will weaken the interaction between starch molecules and improve the flowing ability of starch. When oxidized starch is added, the new hydrogen bonds between starch and oxidized starch are also formed, which weaken the inter- and intra-molecular hydrogen bonds of starch.

Table 1 also shows the influence of OS117% content on the non-Newtonian index *n* of thermoplastic starches. It appears that there is a direct relationship between the content of OS117% and the non-Newtonian index *n*. With the increasing content of OS117%, the non-Newtonian index increases correspondingly (as shown in Table 1). Compared with TPS 30, Non-Newtonian index *n* increases from 0.37 to 0.48 when 10% OS117% is added. It demonstrates that adding OS117% makes the materials more like a Newtonian fluid and also improves its rheological properties. The shear stress versus shear rate data is well fitted with the simple power law model with high coefficients ($r_2 = 0.993–0.998$). The magnitudes of the consistency index (*K*) obtained from the power law model decreases from $10^{4.75}$ to $10^{4.21}$ with the addition of 10 wt% OS117%, as compared to the sample without oxidized starch.

3.3. The influence of temperature on the rheological properties

The temperature has a great influence on the molten flow properties of the mixture. In this study, TPS30 and TPS3OS117% were chosen to investigate the influence of temperature on their rheological properties (shown in Fig. 2). Processing temperatures at 100, 110 and 120 °C were chosen, respectively. As expected, the apparent viscosity decreases with the increase of temperature at a given shear rate. When temperature rises, the chains possess greater energy, and thus the molecular energy of chains increase and the free volume of melting fluid enhance correspondingly. That is, with the increasing temperature, the chain mobility increases and thus the flowing resistance decrease. Therefore, it can be concluded that the flow properties of TPS3OS117% is improved appreciably with the increasing temperature.

3.4. Mechanical properties

Tensile strength, Young's modulus and elongation at break of thermoplastic starches are shown in Table 2. Tensile strength and Young's modulus both decrease with the increasing degree of oxidation of oxidized starch, but on the other hand, the elongation at break is enhanced. Compared with TPS30, the tensile strength of TPS5OS42% decreases from 3.0 to 2.1 MPa, while the elongation at break increases from 126.8% to 131.2%. When oxidized starch content is fixed at 5% (w/w), the elongation at break increases with the increasing degree of oxidation. For example, the elongation at break of TPS5OS70% and TPS5OS117% are 145.0% and 152.5%, respectively. These indicate that the flexibilities of thermoplastic starches are improved with the increasing degree of oxidation of starch, which due to the fact that the addition of oxidized starch disrupts the hydrogen bonds between starch chains. The oxidized starch with a higher degree of oxidation has a stronger interaction between oxidized starch and starch chains, which leads to an increase in the mobility of starch chains.

Table 2
The effect of OS on the mechanical properties of TPS.

Samples	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
TPS30	3.0 ± 0.2	126.8 ± 10.4	41.0 ± 7.0
TPS5OS42%	2.1 ± 0.1	131.7 ± 8.3	44.3 ± 10.7
TPS5OS70%	1.7 ± 0.1	145.0 ± 17.7	30.3 ± 5.0
TPS3OS117%	2.0 ± 0.1	132.6 ± 14.8	31.6 ± 3.2
TPS5OS117%	1.5 ± 0.1	152.5 ± 13.6	22.6 ± 2.6
TPS8OS117%	1.3 ± 0.1	152.5 ± 4.6	21.3 ± 2.4
TPS10OS117%	1.0 ± 0.0	170.2 ± 19.1	18.0 ± 1.8

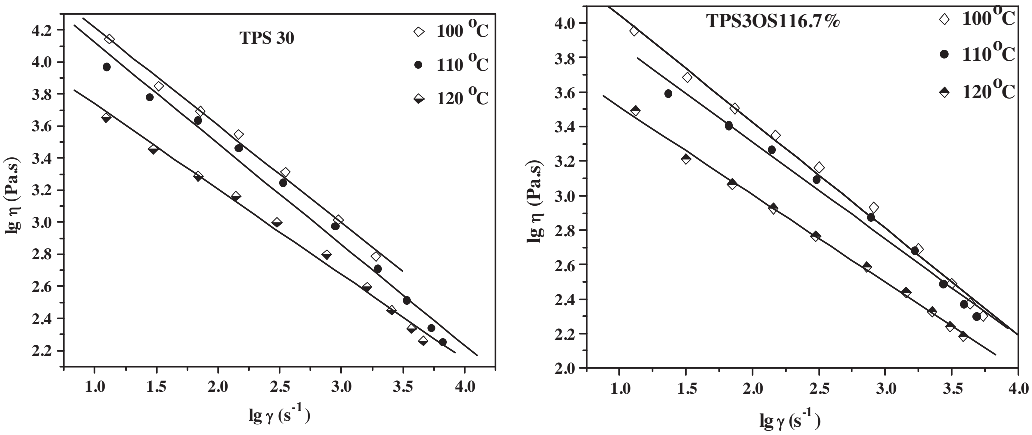

Fig. 2. Rheological curves of TPS30 and TPS3OS117% at different temperatures.

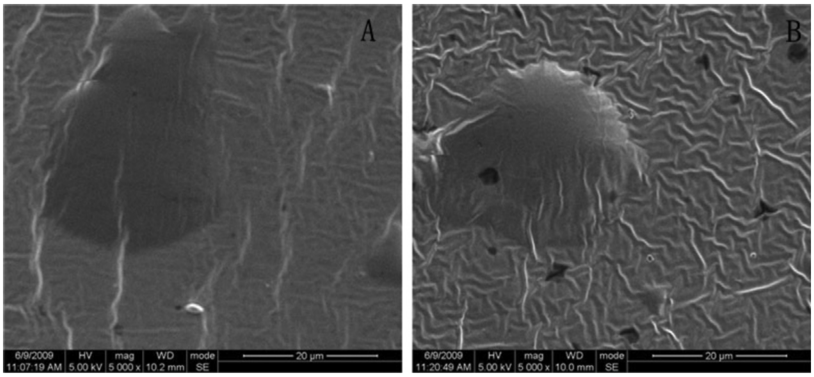

Fig. 3. SEM images of fractured surface of TPS30 (A) and TPS5OS42% (B).

The influence of oxidized starch content on the mechanical properties of thermoplastic starches is shown in Table 2. It is noted that the mixture become more flexible when the amount of OS117% increases. Increasing the amount of OS117% leads to the weaker and softer starch material. The tensile strength and Young's modulus of thermoplastic starches decreases from 3.0 (TPS30) to 1.0 MPa, and from 41.0 (TPS30) to 18.0 MPa, respectively, when OS117% content increases to 10 wt%. While its elongation at break increases from 126.8% to 170.2%, correspondingly. The addition of oxidized starch reduces the tensile strength and Young's modulus, acting like a plasticizer for thermoplastic starches (Willett & Doane, 2002; Zhang et al., 2009), and results in an increasing elongation at break.

3.5. Morphology of thermoplastic starches

The morphology of thermoplastic starches plasticized with glycerol and oxidized starch was examined by SEM. The samples were fractured in liquid nitrogen before testing. Fig. 3A shows the fractured surface of the TPS30 film. The surface is rather smooth, which meant that cornstarch granules were changed to a continuous phase during processing. Due to the cumulative action of plasticizers, high shear rate, and processing temperature, native starch granules melted or were physically broken up into small fragments, which resulted in smoother surfaces and the disappearance of granular structure of cornstarch (Ma, Jian, Chang, & Yu, 2008). No phase separation is observed in Fig. 3B, which demonstrates OS42% is uniformly dispersed in the matrix. This also indicates that there is good compatibility between oxidized starch and native cornstarch. Based on our previous results, the hydroxyl groups of starch were changed to carbonyl and carboxylic acid groups during the oxidization, which took place primarily at the hydroxyl groups at C-2, C-3, and C-6 positions (Zhang et al., 2009). These carbonyl and carboxyl groups of oxidized starch are then available to form strong hydrogen bonds with the hydroxyl groups on starch. In addition, the anhydroglucose ring of oxidized starch is still maintained, so its chemical structure is similar with that of starch, which made a good compatibility with starch illustrated by the good dispersion of oxidized starch in the starch matrix (shown in Fig. 3B). However, this starch based material was so weak to endure the electron beam during characterization and the images become blistered, the phenomenon was also found by others (Mathew & Dufresne, 2002a).

3.6. Dynamic mechanical thermal analysis

The effect of oxidized starches on the storage modulus and glass transition temperature of the thermoplastic starches was studied by dynamic mechanical thermal analysis. As shown in Fig. 4A, the storage modulus of thermoplastic starches decreases when

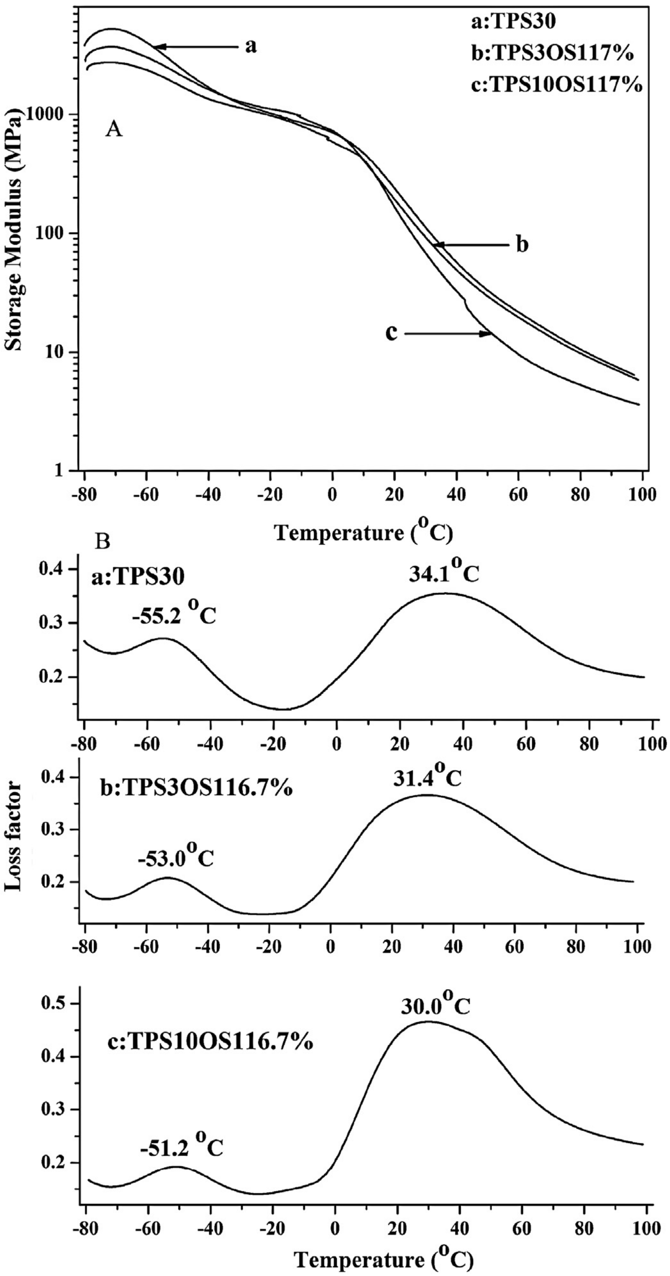

Fig. 4. The dependence of storage modulus and loss factor on the temperature for thermoplastic starch containing oxidized starch.

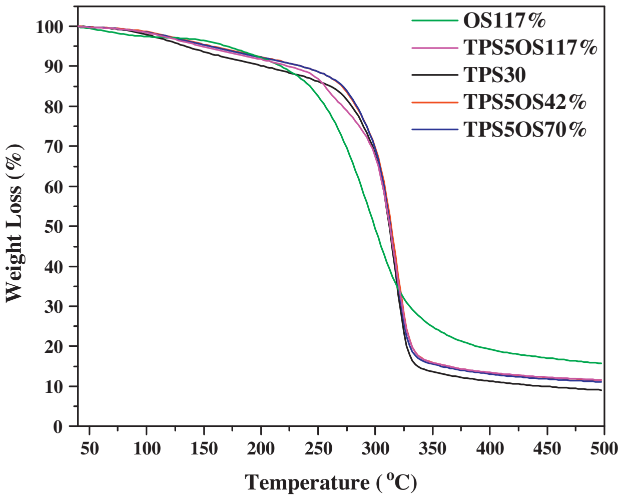

Fig. 5. TG curves of OS117% and thermoplastic starch containing oxidized starch.

oxidized starch is introduced. This phenomenon is ascribed to the strong interaction between oxidized starch and the thermoplastic starch matrix. In general, the storage modulus decreases as the temperature increases. At or above room temperature, the storage modulus of thermoplastic starch blends with oxidized starch was lower than that of TPS30, which is in consistent with their mechanical properties (Thunwall et al., 2006). Fig. 4B shows the loss factor (tan θ) as a function of temperature. In the region corresponding to the maximum loss factor (tan θ), the decrease in storage modulus is very rapid. The loss factor is found to be sensitive to the molecular motion and its peak represents the glass transition temperature. The curve of TPS30 shows two thermal transitions corresponding to the two separate phases in thermoplastic starch, which is reported previously (Angellier et al., 2006; Ma et al., 2008). The lower transition (−55.2 °C) is due to a starch-poor phase (α_1 relaxation) (Angellier et al., 2006). The upper transition (34.1 °C) occurs because of a starch-rich phase (α_2 relaxation), which is regarded as the glass transition temperature (T_g) of TPS30. As far as the thermoplastic starches blends containing oxidized starch are concerned, the upper transitions are shifted to lower temperatures and the lower transition shifted to higher temperatures, and thus the range between these two transition temperatures decrease. It indicates that both starch-rich and starch-poor phases has interactions with oxidized starch, and leads to a better dispersion of the thermoplastic starches as confirmed by SEM study. Compared with TPS30, when 3 wt% OS117% and 10 wt% OS117% is added into the blends, the upper transition temperatures decrease from 34.1 to 31.4 and 30.0 °C, respectively. The lower transition temperatures increase from −55.2 to −53.0 and −51.2 °C, respectively. These results demonstrate that oxidized starch could improve the chain mobility of starch matrix and enlarge the free volume between starch chains.

3.7. Thermal stability

Before preparing thermoplastic starches co-plasticized by oxidized starch, whether oxidized starches would decompose at selected processing temperature are needed to confirm. According to our previous results, they showed that the thermal stabilities of oxidized starches decreased with the increasing degree of oxidation (Zhang et al., 2012). So herein OS117% was chosen to study its thermal stability. $T_{5\%}$ and $T_{10\%}$, which represents the temperature of 5% and 10% weight loss, respectively, are shown in Fig. 5 and list in Table 3. T_{max}, which represents the temperature of maximum weight loss rate, is determined from derivative thermogravimetry (DTG) curves and lists in Table 3. As shown in Table 3, the $T_{5\%}$, $T_{10\%}$ and T_{max} of OS117% are 170, 218 and 299 °C, respectively, which demonstrate that the thermal stability of oxidized starch we used are stable in our processing temperature range.

Table 3
Thermal decomposition temperatures of OS117% and TPS containing OS.

Samples	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)
OS117%	171	218	299
TPS30	134	203	317
TPS5OS42%	157	236	318
TPS5OS70%	156	235	317
TPS5OS117	148	224	317

The thermal stability of thermoplastics starch containing oxidized starch was also investigated by TGA (Fig. 5). The mass loss curves are similar for the thermoplastic starches containing oxidized starch with different degree of oxidization. Because the boiling point of glycerol and $T_{5\%}$ of OS117% is 290 °C and 170 °C, respectively, the mass loss below 100 °C is mainly ascribed to water evaporation, which is present in starch (Ma et al., 2004). As shown in Table 3, the thermal stabilities are improved when oxidized starches were added into the blend. Compared with TPS30, $T_{5\%}$ increases from 134 to 157 °C when only 5 wt% OS42% was added. Furthermore, $T_{5\%}$ of thermoplastic starch is still higher than that of TPS30 when the degree of oxidation further increases to 117%. The reason might be that the presence of oxidized starches improves the binding of water and glycerol to starch, and thus made them more difficult to evaporate during processing. As far as T_{max}s are concerned, the values are unchanged, around 317 °C. On the other hand, oxidized starches are totally decomposed before the maximum decomposition temperature. Therefore, T_{max} belonged to the decomposition of anhydroglucose unit of starch. It is surprising to note that oxidized starch can improve the thermal stability of thermoplastic starches at lower temperature, which means that the addition of oxidized starch prevents the degradation of starch-based materials at the practical processing temperatures.

4. Conclusion

Oxidized starches with high molecular weight and high degree of oxidation are developed to improve the properties of thermoplastic starch herein. When oxidized starch is added into starch matrix, the apparent viscosity decreases. It is found that increasing the oxidized starch content or the degree of oxidization decreases the melting viscosity and non-Newtonian index *n*, which indicates that the flowing fluid behaves more like a Newtonian fluid. The thermoplastic starch blended with oxidized starches exhibit higher elongation at break. The higher carbonyl content of oxidized starch or higher amount of OS117% reduces the stiffness of starch materials. SEM shows the good compatibility between oxidized starch and starch because of the similar molecular structure. The introduction of oxidized starch lowers the storage modulus and glass transition temperature of starch. Compared with TPS30, when 10% OS117% was added, the glass temperature decreases from 34.1 to 30.0 °C. Moreover, the thermal stability of starch based material is improved by adding oxidized starch, i.e. $T_{5\%}$ is increased from 134 °C (TPS30) to 157 °C when only 5% OS42% was added. It can be predicted that this green, low cost starch derivative will also have potential application in other biomacromolecules (e.g. soy protein, cellulose, alginate, and chitin) based materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.03.093.

References

Angellier, H., Molina-Boisseau, S., Dole, P., & Dufresne, A. (2006). Thermoplastic starch-waxy maize starch nanocrystals nanocomposites. *Biomacromolecules*, *7*(2), 531–539.

Averous, L., Fringant, C., & Moro, L. (2001). Plasticized starch–cellulose interactions in polysaccharide composites. *Polymer*, *42*(15), 6565–6572.

Huneault, M. A., & Li, H. (2007). Morphology and properties of compatibilized polylactide/thermoplastic starch blends. *Polymer*, *48*(1), 270–280.

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

Labet, M., Thielemans, W., & Dufresne, A. (2007). Polymer grafting onto starch nanocrystals. *Biomacromolecules*, *8*(9), 2916–2927.

Ma, X., Jian, R., Chang, P. R., & Yu, J. (2008). Fabrication and characterization of citric acid-modified starch nanoparticles/plasticized-starch composites. *Biomacromolecules*, *9*(11), 3314–3320.

Mathew, A. P., & Dufresne, A. (2002a). Morphological investigation of nanocomposites from sorbitol plasticized starch and tunicin whiskers. *Biomacromolecules*, *3*(3), 609–617.

Mathew, A. P., & Dufresne, A. (2002b). Plasticized waxy maize starch: Effect of polyols and relative humidity on material properties. *Biomacromolecules*, *3*(5), 1101–1108.

Onteniente, J. P., Abbès, B., & Safa, L. H. (2000). Fully biodegradable lubricated thermoplastic wheat starch: Mechanical and rheological properties of an injection grade. *Starch – Stärke*, *52*(4), 112–117.

Sarazin, P., Li, G., Orts, W. J., & Favis, B. D. (2008). Binary and ternary blends of polylactide, polycaprolactone and thermoplastic starch. *Polymer*, *49*(2), 599–609.

Sung, J., Park, D., Park, B., Choi, H., & Jhon, M. (2005). Phosphorylation of potato starch and its electrorheological suspension. *Biomacromolecules*, *6*(4), 2182–2188.

Talja, R. A., Peura, M., Serimaa, R., & Jouppila, K. (2008). Effect of amylose content on physical and mechanical properties of potato-starch-based edible films. *Biomacromolecules*, *9*(2), 658–663.

Teixeira, E., Dá Róz, A., Carvalho, A., & Curvelo, A. (2007). The effect of glycerol/sugar/water and sugar/water mixtures on the plasticization of thermoplastic cassava starch. *Carbohydrate Polymers*, *69*(4), 619–624.

Thunwall, M., Boldizar, A., & Rigdahl, M. (2006). Compression molding and tensile properties of thermoplastic potato starch materials. *Biomacromolecules*, *7*(3), 981–986.

Wang, N., Yu, J., Chang, P. R., & Ma, X. (2008). Influence of formamide and water on the properties of thermoplastic starch/poly (lactic acid) blends. *Carbohydrate Polymers*, *71*(1), 109–118.

Willett, J. L., & Doane, W. M. (2002). Effect of moisture content on tensile properties of starch/poly (hydroxyester ether) composite materials. *Polymer*, *43*(16), 4413–4420.

Ma, X. F., Yu, J. G., & Feng, J. (2004). Urea and formamide as a mixed plasticizer for thermoplastic starch. *Polymer International*, *53*(11), 1780–1785.

Xie, F., Halley, P. J., & Avérous, L. (2012). Rheology to understand and optimize processibility, structures and properties of starch polymeric materials. *Progress in Polymer Science*, *37*(4), 595–623.

Zhang, Y. R., Wang, X. L., Zhao, G. M., & Wang, Y. Z. (2012). Preparation and properties of oxidized starch with high degree of oxidation. *Carbohydrate Polymers*, *87*(4), 2554–2562.

Zhang, Y. R., Spinella, S., Xie, W. C., Cai, J. L., Yang, Y. X., Wang, Y. Z., et al. (2013). Polymeric triglyceride analogues prepared by enzyme-catalyzed condensation polymerization. *European Polymer Journal*, *49*(4), 793–803.

Zhang, Y. R., Zhang, S. D., Wang, X. L., Chen, R. Y., & Wang, Y. Z. (2009). Effect of carbonyl content on the properties of thermoplastic oxidized starch. *Carbohydrate Polymers*, *78*(1), 157–161.