



Influence of oxidized starch on the properties of thermoplastic starch



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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.

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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, Dâ 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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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 (H₂O₂, 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 CuSO₄ (0.01% molar ratio based on glucose units of starch) solution and H₂O₂ (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 uniformly. 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_mOS_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)

$$\tau = K\gamma_a^n \quad (1)$$

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

$$\eta = \frac{\tau}{\gamma_a} \quad (2)$$

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:

$$\eta = k\gamma_a^{n-1} \quad (3)$$

$$\lg \eta = \lg K + (n - 1)\lg \gamma_a \quad (4)$$

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.

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