

Effect of Crystal Structure and Hydrogen Bond of Thermoplastic Oxidized Starch on Manufacturing of Starch-Based Biomass Composite

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Starch-based biomass composites were prepared with starch and plant fiber. In order to improve the properties of the composites, oxidized starches (OS) were prepared using hydroxyl peroxide as oxidizer, then glycerol was added into OS as plasticizer to produce thermoplastic oxidized starches (TPOS). Crystal structure, hydrogen bonds of TPOS were researched to gain comprehensive views on the mechanism of the property differences between the starch-based composites with native starch, OS and TPOS. The changes of crystal structure were analyzed by X-ray diffraction analysis. Starch intermolecular hydroxyl changes were investigated using the method of infrared spectrum analysis. It was found that the new hydrogen bonds were formed between the plasticizer, oxidizer and starch, and the starch intermolecular bonding force was weakened. The structure of starch crystallization was destructed in TPOS. Differential scanning calorimetry showed that cross reaction with oxidization and plasticization changed the crystal structure, glass transition process was not observed in TPOS. The tensile and compressive strengths of composite based on TPOS were improved greatly and mechanical properties were not weakened obviously with water content increased. All the results indicated that TPOS could improve the properties of starch-based composites.

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NOMENCLATURE

TPOS = Thermoplastic oxidized starches

OS = Oxidized starches

1. Introduction

Worldwide potential demands for replacing petroleum-based materials by valuable biodegradable polymeric materials are quite significant from the social and environmental viewpoint.^{1,2} Starch-based biomass materials have been produced through mold-foaming process using starch and plant fibers as the main raw materials.³ Starch-based material is one of the most promising materials for biodegradable composites because it is easily available all over the world with a low

price and renewability.⁴ As the main raw material for starch-based composites, starch is one of the most abundant renewable natural biopolymers.⁵ Native starch occurs in the form of discrete and partially crystalline microscopic granules that are held together by an extended micellar network of associated molecules, which make it difficult to melt and combine with plant fibers efficiently.⁶ However, adding plasticizer, such as glycol, glycerol and water, can lower the melting temperature of the native starch.⁷ T. Kunanopparat et al. prepared wheat gluten/glycerol-based materials that were reinforced with natural fiber. They reported that the fiber lignin content influences both the water sensitivity and matrix plasticization of the composite.⁸ Starch/EVOH blends that were reinforced with treated fibers exhibited superior properties compared with neat starch.⁹ Sub Yun et al. researched the compatibility of thermoplastic starch and poly (butylene succinate) and investigated the mechanical properties of thermoplastic starch binary blends.¹⁰ M. O. Rutiaga et al. analyzed the thermoplastic starch matrix

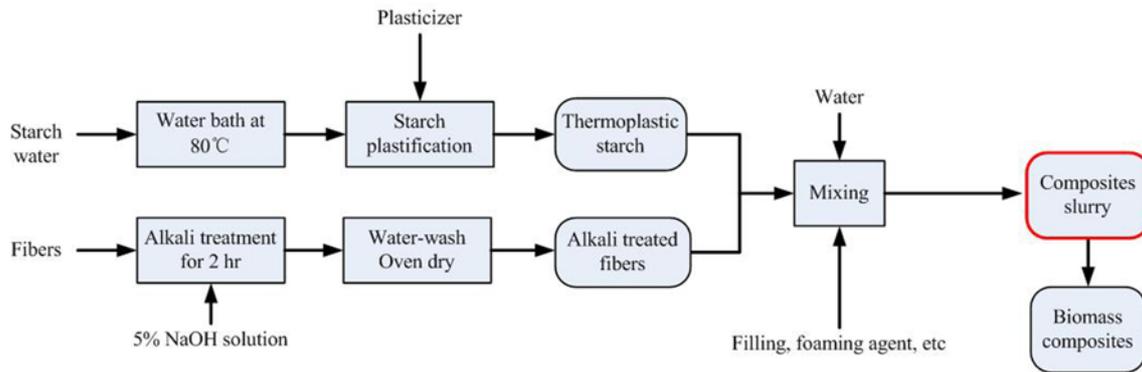


Fig. 1 Technological process flowchart of the biomass composites

binding with the resin in the composite molding process.¹¹ Tensile strength and elongation at break and other mechanical properties of thermoplastic starch-based composites were also researched.¹² The influence of the starch pretreatment process on the physical and chemical properties of starch-based cushion packaging materials were analyzed.¹³ P. Liu et al. revealed that hydrogen bonds exist between TPS and plant fibers in starch-based composites.¹⁴ F. Li et al. studied the micro-mechanism and mechanical properties of thermoplastic starch composites that are reinforced with plant fibers.¹⁵ Jin-Woo Kim et al. investigated the orientation of fibers during the compression molding of fiber reinforced composites.¹⁶ T. Chen et al. used Peleg model curve fitting presented water-absorbing of the composites based on TPS.¹⁷ TPS by itself is a poor choice as a plastic replacement because of its poor mechanical properties and water susceptibility. Therefore, several measures were used to cope with these problems including blends with other biodegradable polymers,¹⁸ modification of the starch structure,^{19,20} reinforcer addition of fibers²¹ and clays,^{22,23} compatibilizer was used to enhance interfacial adhesion of starch, based blends.^{24,25} Hydroxyl peroxide (H_2O_2) was an inexpensive and effective oxidizing agent to prepare oxidized starch (OS).^{26,27} Those method have improved the properties of modified starch, however, crystalline structure of starch is not completely crushed, re-crystallization occurs after water and heat dissipation.

In order to solve the problem above, in this present work, a novel modified method for starch modification, cross-reaction with oxidization and plasticization was developed and applied in biomass composite preparation. The modified starch was thermoplastic oxidized starch (TPOS). X-ray diffraction and differential scanning calorimetry were used to investigate the changes in starch crystallization. Moreover, the changes in microstructure of starch granules and hydroxyl hydrogen bonds between plasticizer, oxidizing agent, and starch molecules were analyzed through infrared spectrum analysis.

2. Experimental Section

2.1 Materials

Straw fiber, with an average length of 6-10 mm and an average diameter close to 100 μ m, was prepared on our laboratory. Wheat starch, with an average particle diameter at about 70 nm, was purchased from Hebei Huachen Starch Sugar Co., Ltd. Talcum powder,

which was used as filling agent, was purchased from Quanzhou Xufeng powder material Co., Ltd. Glycerol and glycol as plasticizing agents were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Hydroxyl peroxide (H_2O_2) with analytical grade (99.5%) as oxidizing agent was purchased from KeLong Chemical Reagent (Chengdu, China). Polyvinyl alcohol (PVA) with purity $\geq 99.0\%$ which was used as adhesive agent, was purchased from Sinopharm Chemical Reagent Co., Ltd. Steric acid as mold-releasing agent, was purchased from Tianjin Guangcheng Chemical Co., Ltd. NaOH was purchased from Yantai Shuangshuang chemical Co., Ltd..

2.2 Oxidation of Starch by Hydroxyl Peroxide

Oxidized starch (OS) was prepared according to the following procession. 200.0 mL distilled water and 40.0 g starch were added in 500 mL round bottomed flask, and the mixture was heated at 78°C for half of hour with mild stirring. Then, 20 mL H_2O_2 was added in the mixture with 160 mL distilled water after the temperature dropped to 25°C, and reacted for 1h. During oxidation, the mixture was stirred vigorously with a mechanical stirring to ensure the H_2O_2 uniformly dispersed in the gelatinized starch. The reaction temperature was kept at 25°C with pH of 7.0. After 24 h, the slurry was dispersed by centrifugation and the products were washed 10 times with 250 mL distilled water.

2.3 Preparation of Thermoplastic Oxidized Starch

Thermoplastic oxidation starch (TPOS) was prepared according to the following procedure. 10% weight ratio of glycerol, 5% weight ratio of glycol and OS were mixed under a high-speed stirring and maintained in a polyethylene bag at 35°C for 12 h. Then the mixture was pressed at 120°C to get 0.5 mm thick films. In order to study the effect of water content on mechanical properties of TPOS, water was added to prepare TPOS according to the same procedure above.

2.4 Manufacturing of the Biomass Composites

As shown in Fig. 1, the technological process of the biomass composites is divided into four phases: fiber treatment, starch modification, mixing and thermo-compression formation.²⁸

In this work, a new biodegradable composite with open cell was prepared using the starch/ fiber composite slurry as raw materials. The raw materials are green. No other wastes were discharged except a large amount of water vapor and a small amount of nitrogen in the

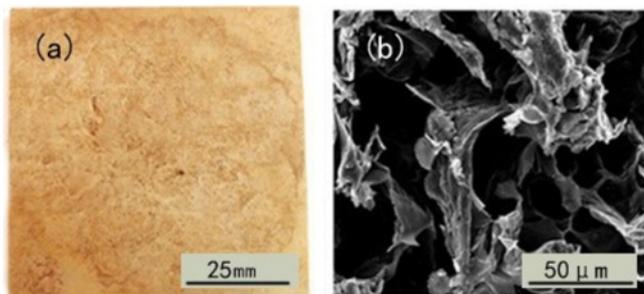


Fig. 2 Surface (a) and the internal structure (b) of the biomass composites

production process. The production process is green. The prepared biomass composites are presented in Fig. 2. The internal structure of the composites was investigated by SEM. Due to the porous structure, the biomass composites could be used in a multitude of applications such as packaging, transportation.

2.5 X-ray Diffraction Experiment

TPOS was dried at 100°C for 12 h in order to prepare anhydrous TPOS. Then, the anhydrous TPOS was ground by using an agate mortar and sieved with 200 mesh sieves. The granule of TPOS was operated at room temperature by using Ni filtered Cu radiation and a curved graphite crystal monochromator. And then the prepared sample was analyzed using XD3 X-ray diffractometer. The slit system was DS/RS/SS = 1°/0.16 mm/1°. The angle (2θ) interval of 5-65° was analyzed at a speed of 5°C min⁻¹.

2.6 The Infrared Spectrum Analysis

About 1 mg of the anhydrous TPOS was mixed with 150 mg of KBr. This mixture was pressed to transparent into pellets under a pressure about 12-14 MPa to prepare sample, then the sample was analyzed using VERTEX-70 FI-IR Spectrometer. The spectra was recorded with a resolution of 2 cm⁻¹ in the range of 400-4000 cm⁻¹.

2.7 Differential Scanning Calorimeter

TPOS (5-8 mg) was heated from 20°C to 100°C within 15 min to eliminate any residual water, and then cooled to 20°C at a cooling rate of 10°C min⁻¹. After that the samples were heated up to 100°C at the same heating rate. Thermal properties of the samples were studied using a German NETZSCH 204 DSC under nitrogen purge. The aluminium pan hermetic pans were used to weigh the starch and TPOS (about 5 mg). Sample pans were performed from room temperature to 400°C at a heating rate of 30°C min⁻¹.

2.8 Moisture Absorption of the Composites with TPOS

The composite samples were dried at 100°C for 4 h and cooled to 20°C in a desiccator, then weighed immediately (M_1). The samples were conditioned in 100% relative humidity at $25 \pm 1^\circ\text{C}$ until a constant weight was obtained and then was weighed again (M_2). The 100% relative humidity was obtained by using closed vessel contained water inside.²⁹ The amount of water absorbed by the samples was calculated by the following formula: water absorption (%) = $(M_2 - M_1) \times 100 / M_1$.

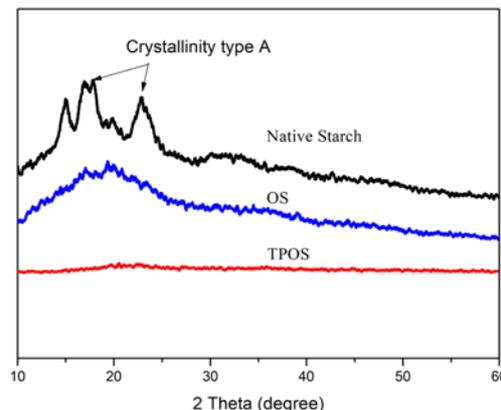


Fig. 3 X-ray diffractograms of native starch, OS and TPOS

2.9 Mechanical Property Testing

Compressive strength experiment: test samples (100 × 100 × 25 mm) were prepared according to GB/T 8168-2008 China. As the standard method A, XYD-15K compression testing machine preloaded 5 N on the specimens; the thickness of specimens was regarded as the original thickness. Tensile strength experiments: according to GB/T 9641-88 China, testing samples (100 × 100 × 5 mm) were prepared. All the measurements were performed for five specimens and averaged.

3. Results and Discussions

3.1 X-ray Analysis

Fig. 3 shows X-ray diffractograms of native starch, OS and TPOS. Analysis of native starch showed predominance of crystallinity type A, whose diffraction peaks were located at $2\theta = 15.5^\circ, 18.2^\circ, 23.4^\circ$.⁵ OS diffraction peak was located at $2\theta = 20.3^\circ$, proving that its crystallinity type is not type A. By fitting calculation using Jade software, computed NS crystallinity index was 19.95%, and crystallinity index of OS decreased to 11.3%. Significantly, visible diffraction peaks were not observed in XRD pattern of TPOS. These proved that the crystalline order observed in the starch granules was completely destroyed in TPOS. The crystallinity index of TPOS was 0.85% by calculation. Therefore, it was indicated that the plasticizer molecules and hydroxyl peroxide molecules obstructed starch molecules. With the breaking of crystal structure in TPOS, the problem of starch re-crystallization that restricted mechanical properties of the starch-based composites was solved to some extent.³⁰

3.2 Infrared Spectrum Analysis on TPOS

Hydrogen bonds are easily formed between O-H groups. The O-H stretching vibration frequency moves to a lower frequency when the O-H groups form a new hydrogen bond in the compound molecule. The stronger the hydrogen bond formed between O-H groups, the more the stretching vibration frequency shifts to lower levels.^{31,32} Fig. 4 illustrates changes in the frequency and absorbance in the region of hydroxyl group vibrations of native starch, OS and TPOS. In Fig. 4, it was revealed that the hydroxyl peroxide drove the absorption peaks of hydroxyl group (3400.5 cm⁻¹) toward to the lower frequency (3381.2 cm⁻¹). And the cross reaction of oxidation and plasticization

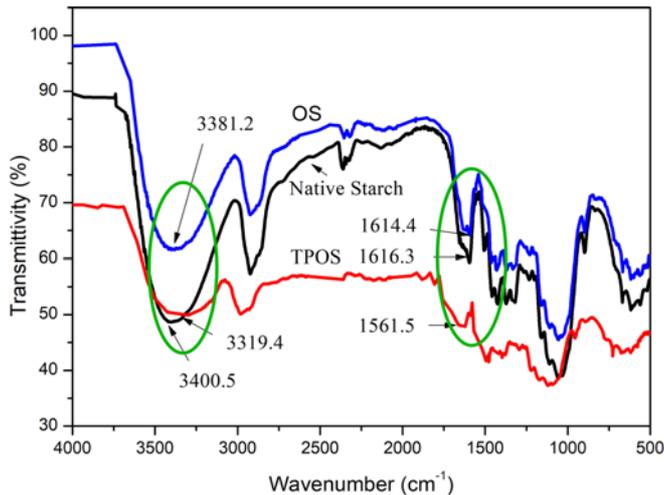


Fig. 4 The infrared spectra of native starch, OS and TPOS

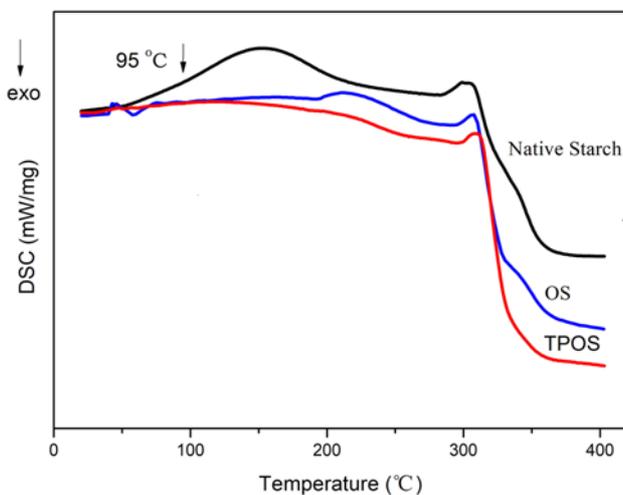


Fig. 5 DSC curves of Native starch, OS and TPOS

brought more change, which reduced the frequency to 3319.49 cm^{-1} . According to the experimental result, the glycerol, hydroxyl peroxide, and starch molecules formed stronger hydrogen bonds on O-H of thermoplastic oxidized starch. Remarkably, the frequency ($1620\text{--}1540\text{ cm}^{-1}$) of carbonyl group (COO) had a significant change. The peak of thermoplastic oxidized starch showed a decreasing trend in the range of the frequency ($1620\text{--}1540\text{ cm}^{-1}$). Plasticization introduced the carbonyl group into OS chains. It was testified that glycerol molecular was easier to combine with starch molecules on the basis of oxidation reaction.

3.3 Thermal behavior of TPOS

DSC curves of native starch, OS and TPOS are shown in Fig. 5. In the temperature range ($50\text{--}150^\circ\text{C}$), DSC curves of native starch show an increasing trend, which means that absorption of heat occurred. This is attributed to the depolymerization reaction with the temperature increasing. It could be seen that the glass transition temperature (T_g) of native starch was 95°C . When the gelatinized starch was oxidized by hydroxyl peroxide, the hydroxyl group of starch was transformed to

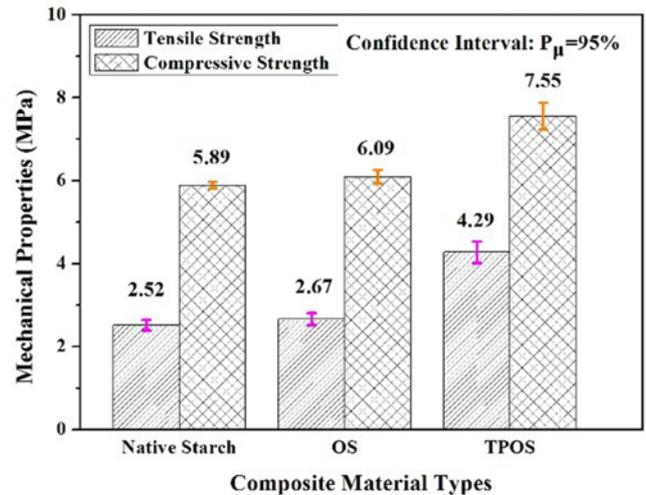


Fig. 6 Mechanical properties of the different biomass composites based on native starch, OS and TPOS

carbonyl group. As a result, the hydrogen bonds among starch molecules was weakened, leading to starch lose its original crystallization. Therefore, the T_g of OS was increased. From the DSC curve of TPOS, the endothermic peak was not observed in the temperature range ($50\text{--}150^\circ\text{C}$). TPOS didn't have T_g temperature. Plasticization introduced the carbonyl group into oxidized starch chains. These proved that cross reaction with oxidation and plasticization changed the crystallization structure. The phenomenon confirmed that retrogradation didn't existed in thermoplastic oxidized starch.³³

3.4 Mechanical Properties of Composites Based on Native Starch, OS and TPOS

Fig. 6 shows that the results of tensile and compressive strength tests on the composites that based on native starch, OS and TPOS. The results presented that the compressive strength was larger than tensile strength of the composites, no matter how different of starch types. It also was testified that the mechanical properties of composite based on OS was better than composite based on native starch. And the changes were not obvious. However, the tensile and compressive strength of composite based on TPOS were improved greatly. The tensile strength was increased from 2.52 MPa to 4.29 MPa , and the compressive strength was enlarged from 5.89 MPa to 7.55 MPa . The reasons explained why biomass composites that based on TPOS had high tensile and compressive strength were that the intermolecular hydrogen bonds were stronger between plant fiber molecular chains and thermoplastic oxidized starch chains. As the cross reaction with oxidation, plasticization and starch molecular changed the crystallization structure of starch. The problem of retrogradation was solved in some extent, which is the bottleneck problem that restricted the properties of starch-based biomass composites.

3.5 Effect of Oxidization, Plasticization on Moisture Resistance of the Starch-Based Biomass Composites

Starch easily absorbs moisture in the environment, which leads to the mechanical properties decrease sharply of starch-based biomass composites. In this section, moisture resistance of the composites with

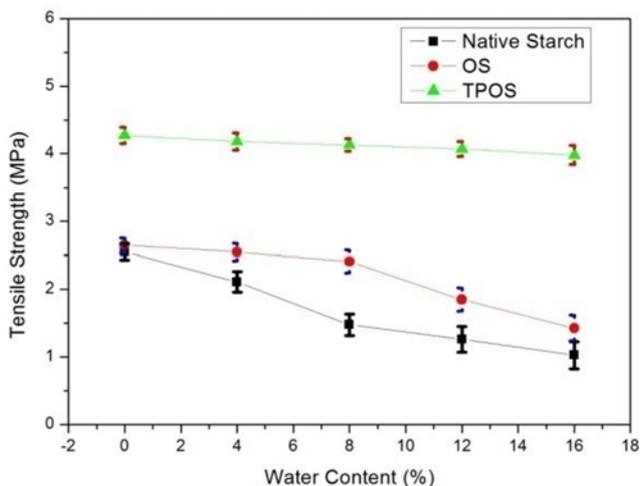


Fig. 7 Tensile strength of the composites with different water content

different starch types was studied. The results are shown in Fig. 7. With water content increasing, tensile strength of the composites based on native starch was decreased. When water content was lower, the change of tensile strength was not obvious in composites based on OS. However, when water content increased to 8% and more, the tensile strength was decreased shapely. Therefore, moisture resistance of the composites that based on OS was not great. Oxidation can't solve the moisture absorption problem of starch-based composites. It could be seen clearly that mechanical properties were not weakened obviously with water content increasing in the TPOS-based composites. The tensile strength was changed from 4.27 MPa to 3.98 MPa. The phenomenon revealed that the composites that based on TPOS had great moisture resistance property.

4. Conclusions

X-ray diffraction and DSC analysis showed that reaction of plasticization and oxidation destroyed the crystalline structure of starch. Starch loses its original crystallization. The problem of starch retrogradation was solved in some extent.

Infrared spectrum analysis observed that the new hydrogen bonds were formed between the plasticizer, oxidizer and starch. Plasticization introduced the carbonyl group into OS chains.

TPOS improved the mechanical properties of starch-based biomass composites, while the composites that based on OS did not present significantly improvement. Tensile strength of TPOS-based composites was not weakened obviously with water content increasing, proving that the moisture resistance property of the TPOS-based composites was great.

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