



# Research on Rheological Behavior of Biobased Composite Slurry Composed of Sisal Fiber and Thermoplastic Oxidized Starch

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In this work, a biobased composite was prepared via foam molding. The prepared composite contained plant fibers as main raw materials, thermoplastic oxidized starch (TPOS) as binder, and several additives as active agents. A novel modified method for starch, combination of oxidation and plasticization, was developed and applied in the preparation of biobased composites. Rheological property is the main physical quality of interest in the industrial production of biobased composites. The influence of starch modification on the rheological properties of the biobased composite slurry was analyzed using digital rotational viscometer. Results showed that modification of starch decreased the viscosity of the composite slurry significantly. Moreover, inherent reasons of the change was analyzed. X-ray diffraction revealed that crystalline structures were completely destroyed in TPOS. Infrared spectrum analysis showed that sisal fibers formed hydrogen bonds with TPOS. The starch became compatible with plant fibers, thus decreasing the viscosity of the slurry. Furthermore, the effect of different plasticizer mass ratios on the rheological behavior of the slurry was investigated to determine the optimal plasticizer/oxidizer mass ratio for industrial manufacturing. A 10/0.68/1.36 mass ratio of starch/oxidizer/plasticizer had the best effect on the viscosity of the composite slurry.

**Keywords:** Biobased Composites, Thermoplastic Oxidized Starch, Sisal Fiber, Rheological Behavior, Hydrogen Bond.

## 1. INTRODUCTION

Biobased composites are made by sisal fibers, thermoplastic oxidized starch (TPOS), foaming agent and active agents via foam-molding process. Biobased composites are environment-friendly materials, with extensive raw material sources, simple processing, and non-polluting production cycle.<sup>1–3</sup> Due to their cellular structure, acoustic absorption and cushioning properties, biobased composites are used in a multitude of different applications, including transporting, packaging, as well as indoor decorations. In industrial production of biobased composites, the rheological property is one of the main physical quantities in calculating the friction resistance during the transport of biobased composite slurry.<sup>4,5</sup> In the actual production process, treated sisal fibers and various additives are incorporated into thick slurry by stirring.<sup>6</sup> This kind of slurry has high viscosity as it contains abundant plant fibers. The high viscosity hinders the flowing of the slurry which

causes problems by using pipelines to transport materials in the production line. This became a bottleneck that limits the productivity.<sup>7,8</sup> As the main ingredient of these biobased composites, plant fibers and native starch can't be compatible, they have few interactions in their natural conditions. Starch modification is a significant processing for the preparation of biobased composites with excellent mechanical properties.<sup>9,10</sup> Given that starch modification promotes the industrialization of biobased composites, the influence of starch oxidation and plasticization on the rheological properties of biobased composite slurry should be investigated.

Many scholars have carried out researches on the rheological properties of biobased composites. The melting behavior of starch complied with the Power Law equation and its viscosity decreased with the rise of temperature and humidity ratio.<sup>11,12</sup> And the flow behavior of thermoplastic starch in the process of extrusion was analyzed by pseudo plasticity. Regardless of thermoplastic starch was, it showed stick wall flow behavior in the presence of a large number of glycerin or other small molecule

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additives.<sup>13,14</sup> Scholars focused on optimization of rheological properties of starch slurry, quantitative model by the rheological behaviors and the effects of the fibers space-grid structure on the viscosity.<sup>15,16</sup>

However, the influence of the variation of molecule structure before and after starch modification on rheological properties were rarely studied. Limited attention has been made on the deep-seated reason behind the change of rheological properties after oxidation and plasticization. The influence of the starch molecules change on rheological properties were analyzed in this paper. And the deep mechanism of this change was revealed. In the presented work, a digital rotational viscometer was used to study rheological properties of the biobased composite slurry. X-ray analysis, scanning electron microscopy was used to investigate the microstructure changes aim to present the reasons of the effect of starch modification on viscosity. Lastly, rheological model of the slurry was developed, and the optimal rheological parameters for the pipeline transportation of biobased composites were explored.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials and Equipment

The main raw materials were as follows: self-made sisal fibers with an average length of 6–10 mm; corn starch with an average particle diameter of approximately 70 nm (Hebei Huachen Starch Sugar Co., Ltd.); talcum powder with a 400-mesh particle size (Quanzhou Xufeng Powder Material Co., Ltd.) as filling; analytical grade glycerol and glycol (Tianjin Fuyu Fine Chemical Co., Ltd.) as plasticizing agents; polyvinyl alcohol with purity  $\geq 99.0\%$  (Sinopharm Chemical Reagent Co., Ltd.) as adhesive; analytical grade steric acid (Tianjin Guangcheng Chemical Co., Ltd.) as mold-releasing agent; and analytical grade sodium hydroxide (Yantai Shuangshuang Chemical Co., Ltd.).

### 2.2. Formulation of Biobased Composites

As shown in Figure 1, the production process of biobased composites has four phases: fiber treatment,<sup>6,17</sup> starch modification, mixing and thermo-compression formation.

The TPOS was prepared according to the following procedure: 200.0 ml distilled water and 50.0 g starch were combined in 500 ml round-bottomed flask, and the mixture was then heated at 80 °C for 30 min with mild stirring.<sup>18</sup> Then, 160 ml distilled water was added to the mixture with 5.0 g of  $\text{H}_2\text{O}_2$  after the temperature decreased to 25 °C. The mixture was allowed to react for 1 h. During oxidation, the mixture was vigorously mechanically stirred to ensure the uniform dispersion of  $\text{H}_2\text{O}_2$  in the gelatinized starch. The reaction temperature was kept at 20 °C with pH of 8.0. After 24 h, the slurry was dispersed via centrifugation and washed 10 times with 250 ml distilled water; afterward, 10 g plasticizer, and oxidized starch (OS) were mixed under high-speed stirring and maintained in a polyethylene bag at 80 °C for 2 h. The plasticizer was glycerol and glycol, and mass ratio of glycerol/glycol was 2/1.<sup>19,20</sup> TPOS and the sisal fiber were mixed to obtain a slurry. The slurry was injected into a hot mold via thermo-compression foaming to produce the biobased composite material. And a biobased composites products, mobile phone packaging was presented in Figure 2. In preparation process of the biobased composite, the rheological property is one of the significant quantities in calculating the friction resistance when the slurry is transplanted.

### 2.3. Measurement of Rheological Properties with a Digital Rotational Viscometer

A digital rotational viscometer (Type: DV-79 + pro) was used in this test. F type rotor was chosen as test rotor. The speed was set at  $150 \text{ r} \cdot \text{s}^{-1}$ . The digital rotational viscometer was equipped with a hydraulic pump for controlling the temperature of the water bath. The viscometer could be programmed for rheological measurement. The viscometer was preheated to 85 °C and left idle for 6 seconds to obtain stable data. Samples were placed into the test tube and the rotor was turned on to reduce experimental error. Each measurement was repeated 10 times and the average value was taken as the final value. The time interval of each data was 6 seconds and the program was repeated five times. After data collection, the rheological characteristic curve was drawn after deleting unreliable data points.

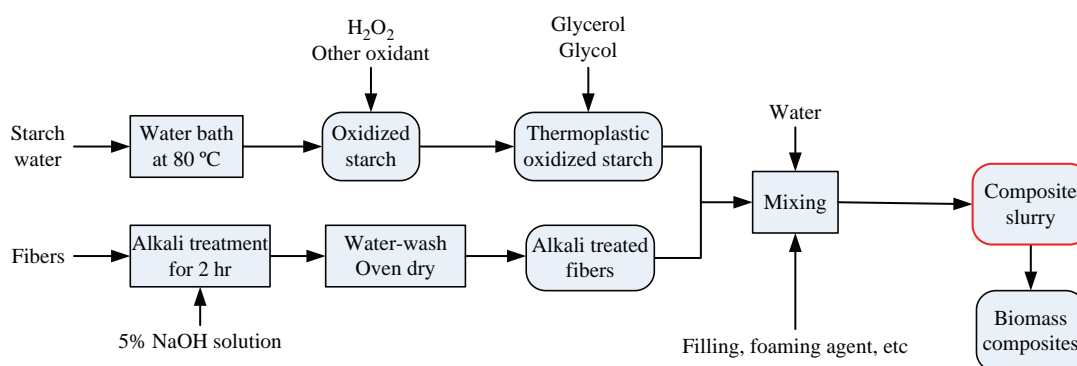
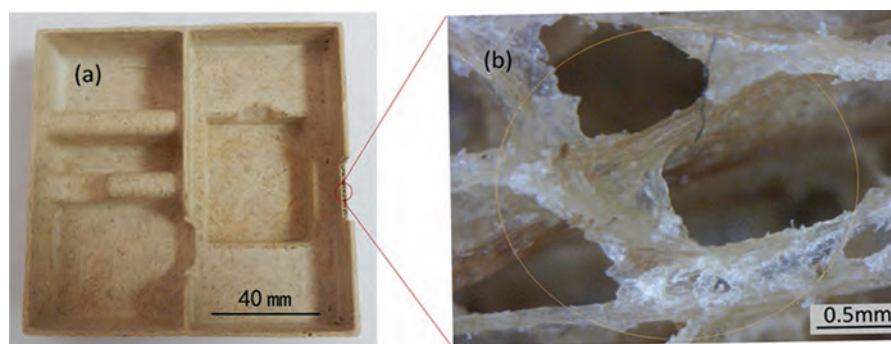


Fig. 1. Flowchart of technological process of biobased composites.



**Fig. 2.** (a) Product of biobased composites, mobile phone packaging; (b) internal structure of biobased composites.

Rotor shear rate was set at  $130 \text{ s}^{-1}$ . The temperature was set at  $5^\circ\text{C}$ . Experimental data was collected every 0.2 seconds. The stable shear stress value was recorded. When the data was stable, the temperature was re-adjusted to 25, 45, 65, and  $85^\circ\text{C}$ . After repeating the above-mentioned tests, the rheological characteristic curve was drawn after deleting unreliable data points. The shear rate was re-adjusted respectively to 130, 135, 140, 145, and  $150 \text{ s}^{-1}$ . After repeating the above-mentioned tests, the stable data was recorded.

#### 2.4. X-ray Diffraction Experiment

TPOS was dried at  $100^\circ\text{C}$  for 24 hs in order to remove moisture. Then, the anhydrous TPOS was ground by using an agate mortar and filtered with a 200 mesh sieve. The compacted sample was flat. The assay was operated at room temperature by using Ni-filtered Cu radiation and a curved graphite crystal monochromator. And then analyzed using XD3 X-ray diffractometer. The slit system was  $\text{DS/RS/SS} = 1^\circ/0.16 \text{ mm}/1^\circ$ . The angle ( $2\theta$ ) interval  $5\text{--}65^\circ$  was analyzed at a speed of  $5^\circ\text{C min}^{-1}$ .

#### 2.5. Scanning Electron Microscopy

The spatial structure of biobased composite slurry was investigated using scanning electron microscope (SEM) FEG250 with an acceleration voltage of 10 kV. Prior to SEM observation, all samples were mounted with carbon tape on aluminum stubs and sputter coated with gold to make them conductive.

### 3. RESULTS AND DISCUSSION

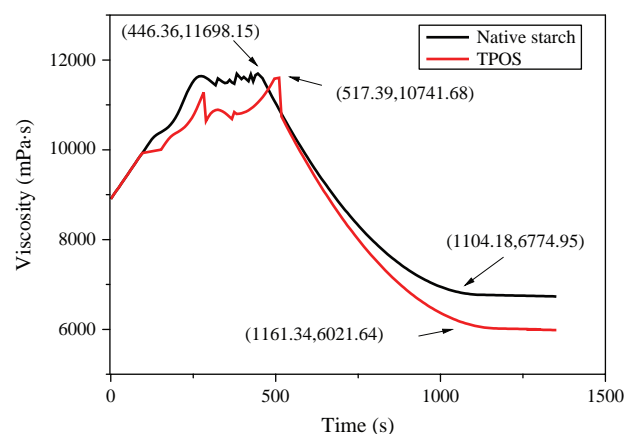
#### 3.1. Viscosity of the Biobased Composite Slurry

The rheological properties of the biobased composite slurry were investigated using a digital rotational viscometer as shown in Figure 3. TPOS was prepared with glycerol and glycol as plasticizers, with the mass proportion of starch/oxidizer/plasticizer of 10/1/2.<sup>21,22</sup> The viscosity of biobased composites slurry first increased, gradually decrease, and then stabilized over time. Most fibers were chaotically arranged at the beginning time, the axial orientation of the fibers was inconsistent with the direction of

the shear force. Moreover, when shear force was applied on the fibers, fluid power promote fibers more chaotic. Hence, viscosity increased at the beginning of stirring. The viscosity of the biobased composite slurry peaked at approximately 245 s and then fluctuated because of the uneven force and short sharp swings of the rotor under high viscosity. Then the viscosity of the biobased composite slurry gradually decreased because of orientation of the fibers was arranged into single orientation by stirring. The viscosity tended to be stable after 1100 seconds. Moreover, the viscosity of the TPOS-based slurry and native starch-based slurry was respectively  $6774.95 \text{ mPa}\cdot\text{s}$  and  $6021.64 \text{ mPa}\cdot\text{s}$ , when the viscosity was stable. The viscosity of TPOS-based composite slurry was smaller than the viscosity of native starch-based composite slurry.

#### 3.2. Influence of Starch Modification on Rheological Behavior

Starch modification influenced the rheological properties of the biobased composite slurry and decreased the viscosity according to the results in 3.1. In order to further explore the fundamental reasons for this effect, the starch microstructure changes has been researched through following X-ray analysis and SEM.



**Fig. 3.** The curve of the viscosity to time of the biobased composite slurry.

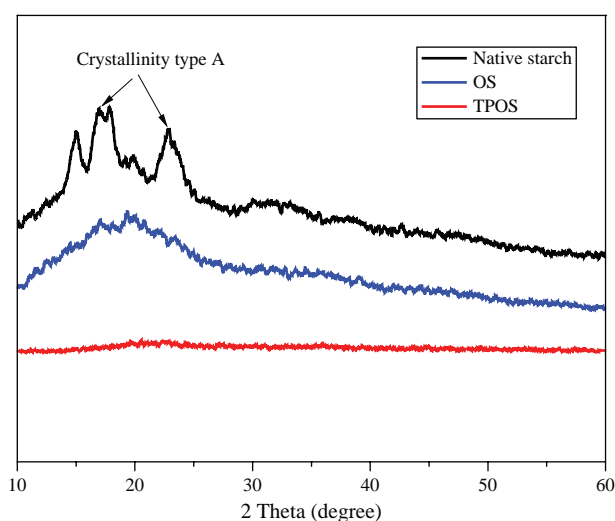


Fig. 4. X-ray diffractograms of native starch and TPOS.

### 3.2.1. X-ray Analysis of TPOS

The recorded XRD patterns for native corn starch, OS and TPOS were shown in Figure 4. These results revealed important changes in starch structure after plasticization. The diffraction peaks of native starch were located at  $2\theta = 15.1^\circ$ ,  $18^\circ$ ,  $23.1^\circ$ . The analysis of native starch displayed a predominance of crystallinity type A. Mixing with hot water gelatinized native starch and destroyed the crystal structure of starch. However, starch would retrograde when the water was lost and the temperature decreased. A crystal diffractogram peak was found in the X-ray diffractogram of OS. The formation of B- and V-type crystal structures occurred in OS because of starch recrystallization. After processing with the plasticizer, the crystal structure of starch clearly changed, as shown by X-ray diffractograms. Diffraction peaks were not found in the X-ray diffractogram of TPOS. These findings proved that the crystal state of the native starch granules was completely destroyed in TPOS.

### 3.2.2. Microstructure Changes the Biobased Composite Slurry

Figure 5 presented the SEM images of the biobased composite slurry with native starch and TPOS. Fibers were

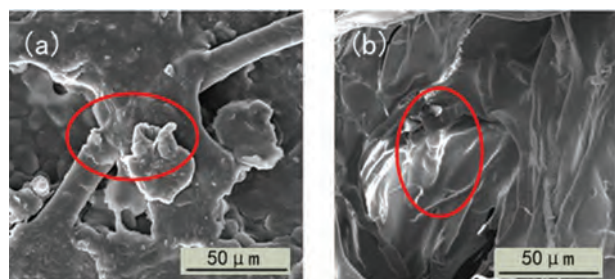


Fig. 5. SEM of the biobased composite slurry with (a) native starch and (b) TPOS.

distributed in an interchange network structure in the biobased composite slurry. Obviously, native starch combined with plant fibers hardly, starch and plant fibers were incompatible, starch agglomerated independently. However, it was shown that TPOS adhered to the surface of plant fiber tightly in the SEM of slurry with TPOS. And the TPOS had a tight bond with fibers, which proved the existence of a complex internal force in the TPOS-based composite slurry. The changes in the molecular structure in starch after starch modification were fundamental reasons for strong adherence of TPOS with sisal fibers. The oxidation of  $H_2O_2$  transferred the electrons of hydrogen atoms in native starch molecules to the oxidizer. Given that the electron-depleted H atom had a particularly small size, the other electronegative atoms such as  $O^-$  and  $N^-$  can get quite close to these highly polar  $H^+$  groups and thus experience an unusually strong field. The resulting bond was known as the hydrogen bond. Alkalization caused the hydrogen atoms in the sisal fibers to lose electrons. The hydrogen atoms in the sisal fibers were alkalized by sodium hydroxide with highly polar  $H^+$ . Therefore, sisal fibers formed hydrogen bonds with TPOS. The hydrogen bonds was proved by infrared spectrum analysis as shown in Figure 6. The O–H stretching vibration frequency moved to a lower frequency when the O–H group formed a new hydrogen bond in the compound molecule. The stronger the hydrogen bond formed between O–H groups, the more the stretching vibration frequency shifted to low levels.<sup>23,24</sup> It was revealed that the hydroxyl peroxide drove the absorption peaks of hydroxyl group (3404.3) to move toward to the lower frequency (3372.4) in Figure 6.

These hydrogen bonds made the starch stick to the surfaces of fibers. Starch molecules and plant fibers become compatible. Therefore, the viscosity of TPOS-based composite slurry decreased significantly.

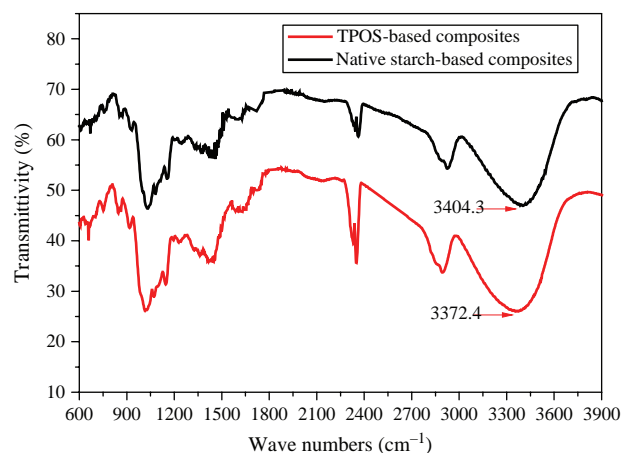


Fig. 6. The infrared spectra of TPOS-based and native starch-based composites.



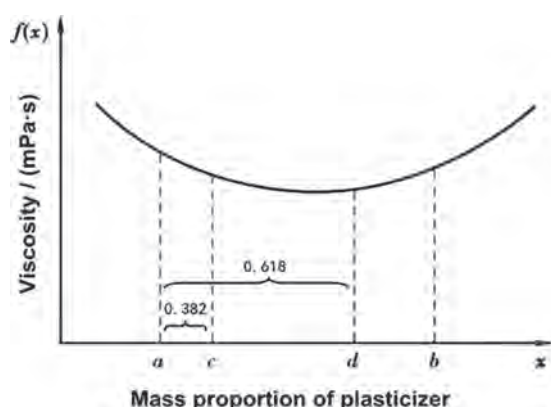


Fig. 7. Optimization principle diagram of golden section search method.

### 3.3. Optimization of Plasticizer Proportion and Analysis of the Rheological Model

Starch modification influenced the rheological properties of the biobased composite slurry. The addition of plasticizer and oxidizer decreased the viscosity of the slurry, which was analyzed in above. Plasticizer/oxidizer proportion was optimized based on the rheological properties of the slurry in the following research.

The optimization principle diagram of the golden section search method was shown in Figure 7. The initial optimization interval was selected as  $a$  to  $b$ . If  $f(c) < f(d)$ , new optimization interval became  $c$  to  $b$ . If  $f(c) > f(d)$ , then the new optimization interval became  $a$  to  $d$ ,<sup>25</sup> and so on until the optimal result was searched. Starch modification of oxidization and plasticization would decrease the viscosity of the slurry, if the mass proportion of modifying agents was proper. However, the viscosity would develop in the opposite direction when plasticizer and oxidizer content became extreme. The golden section search method was used to solve optimization problems by modifying agent proportion based on the rheological properties of the slurry.

Based on the above analysis, the viscosity of native starch-based slurry without modifying agent was 6774.95 mPa·s, and the viscosity of TPOS-based composite slurry added plasticizer with the mass proportion (starch/oxidizer/plasticizer) of 10/1/2 was 6021.64 mPa·s. Further experiments showed that the viscosity of the slurry with the mass proportion (starch/oxidizer/plasticizer) of 10/2/4 was 6722.43 mPa·s. Therefore, the initial optimization interval was chosen that no plasticizer to the mass proportion (starch/oxidizer/plasticizer) of 10/2/4. According to golden section search method, viscosities of the TPOS-based slurry with different mass proportion of plasticizer were investigated, and the results were presented in Table I. The optimal interval of mass proportion of plasticizer was (starch/oxidizer/plasticizer) 10/0.678/1.356 to 10/0.684/1.368, and the viscosity of the TPOS-based composite slurry based on the optimal mass proportion of plasticizer was 4281.67 mPa·s.

Table I. Viscosity of the TPOS-based slurry with different mass proportion of plasticizer.

Group number	Mass proportion of plasticizer (starch/oxidizer/plasticizer)	Viscosity/(mPa·s)	Remark
1	10/0.764/1.528	5885.76	Less
	10/1.236/2.472	6451.32	
2	10/0.472/0.944	6578.52	Less
	10/0.764/1.528	5885.76	
3	10/0.764/1.528	5885.76	Less
	10/0.944/1.888	5989.23	
4	10/0.652/1.304	5185.78	Less
	10/0.764/1.528	5885.76	
5	10/0.584/1.168	5532.36	Less
	10/0.652/1.304	5185.78	
6	10/0.652/1.304	5185.78	Less
	10/0.695/1.39	4427.51	
7	10/0.695/1.39	4427.51	Less
	10/0.721/1.442	4764.14	
8	10/0.678/1.356	4281.67	Less
	10/0.695/1.39	4427.51	
9	10/0.668/1.336	4401.77	Less
	10/0.678/1.356	4281.67	
10	10/0.678/1.356	4281.67	Less
	10/0.684/1.368	4293.54	

## 4. CONCLUSIONS

This research analyzed the effect of starch modification on the rheological properties of biobased composite slurry. The results of this study will benefit any future research on the rheological behavior of composite slurry, as well as aid in the industrialization of biobased composites.

The viscosity of the slurry first increased, then decreased, and finally stabilized over time. The viscosity of TPOS-based composite slurry was smaller than the viscosity of native starch-based composite slurry.

The crystalline structure of the starch was completely destroyed in TPOS. Moreover, sisal fibers formed hydrogen bonds with TPOS. These hydrogen bonds made starch become compatible with sisal fibers, which decreased the viscosity of the biobased composite slurry.

When the mass ratio of starch/oxidant/plasticizer was 10/0.68/1.36, the cross-reaction of plasticization and oxidization had the best effect on the viscosity of the biobased composite slurry.

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