Research on Influencing Factors on Rheological Properties of Chitosan/Starch Film Slurry

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Abstract: In order to improve the industrial production efficiency of chitosan/starch film, reducing slurry rheology is an important measure. This paper explored that the temperature, chitosan starch ratio, plasticizing different components had a great impact on the rheology of the slurry. As the starch content and temperature increased, the rheology of the slurry first decreased and then increased. Finally, it was determined that when the slurry was transported at 60\degree C with chitosan: starch =1:1.5 and only the chitosan was plasticized, the viscosity was the minimum. The viscosity of the slurry was related to the hydrogen bond formed by the slurry. The more hydrogen bonds, the greater the viscosity. Plasticizing chitosan destroyed the crystal structure and facilitated the formation of the network structure, which was conducive to the shear flow of the slurry.

1. Introduction
Packaging materials, prepared by petroleum derivatives, has caused huge environmental pollution in various industries, such as the plastic rubber and so on. It becomes solid waste and eventually causes great trouble to people\'s production and life with the aging of use, [1]. Therefore, the current research is focused on the development of degradable green packaging materials. In packaging materials, antibacterial packaging due to its inhibition of microorganisms was known as a promising development direction for packaging materials [2]. In the previous study, the chitosan has been widely used in antimicrobial packaging materials because its proven biocompatibility [3] and antimicrobial activity [4]. And the starch has been regarded as the frequently-used degradable materials because of its convenient preparation and abundant reserves [5]. We usually mix these two materials to overcome the shortcomings of the bad mechanical properties of the chitosan film and the starch film. [6]. Therefore, it has a good application effect and a broad market prospect by regarding the chitosan-starch mixed film as antibacterial packaging material.

The industrial production of chitosan-starch film often adopts the technology of jostling, blowing and molding. The slurry was often attached to the surface of the pipe, which made it difficult to...
control in the process of transportation. In addition, the rheological property is an important parameter of slurry in the industrial production of composite products, and also one of the main physical quantities to calculate the friction resistance of pipeline in the design of automatic transportation equipment of slurry production line [7]. In order to better improve the processability of composite films, it was of great significance to study the rheological property of mixed slurry. The research results of many scholars at home and abroad have confirmed that temperature and self-concentration have an effect on the rheological property of slurry [8].

In order to improve the performance of the composite film as well as make a better compatible of starch and chitosan, the researchers are also exploring different modification methods such as glycerol [9], glutaraldehyde [10], mustard oil [11] and polydopamine [12] to optimize the film properties.

Many scholars have already made a lot of explorations on the slurry of biomass material. Willett et al. found that the melting behavior of starch in the extruder obeyed the power law formula, and the melt viscosity decreases with the increase of temperature and moisture content [13]. A Silva-Weiss et al. studied the effect of murta leaf on the rheology property of chitosan-starch mixed slurry [14]. Aichholzer et al. used pseudoplasticity and viscosity to describe the flow behavior of thermoplastic starch during extrusion. It was concluded that no matter what kind of thermoplastic starch, it showed the flow behavior of adhesive wall in the presence of a large amount of glycerol or other small molecular additives [15]. Zhang et al. studied the effect of plasticized oxidation composite modification on the rheological property of biomass slurry, and the effect of composite modification on the rheological property of starch slurry was introduced in detail from the microscopic point of view [16].

In summary, scholars mainly explore the rheological behavior of composite slurry from the point of view of quantitative model of rheological behavior, external factors and rheological optimization. There was a shortage of studies analyzing the effects before and after modification on what the molecular structure change has made to the rheological property and people don’t make an in-depth inquiry on the root causes for the change of rheological property of plasticizing modification. Therefore, the main purpose of this article is to explore the effect of single-whole plastic modification on the rheological properties of chitosan-starch film by means of plasticization and separation. And the effects of modification of single/integral plasticization on the rheological properties of the slurry were characterized by scanning electron microscopy, infrared spectroscopy, X-ray diffraction (the following three test torches were referred to as SEM/XRD/FTIR) and other experimental methods to explore the mechanism of the influence of plasticizing modification on the rheological properties of the mixed slurry.

2. Experiment

2.1. Experimental instruments and materials
Glycerin and ethylene glycol (99% purity) were purchased as plasticizers from Tianjin Fuyu Fine Chemical Co., Ltd.; Corn starch, reagent grade, average particle diameter 70nm, Hebei Huachen Starch Sugar Co., Ltd.; Chitosan (95% deacetylation degree), Shandong Dongrun Biotechnology Co., Ltd.; Urea, AR, purity ≥99.0%, Tianjin Zhiyuan Chemical Reagent Co., Ltd.; NaOH powder, purity ≥96.0%, Cangzhou Manyue Chemical Sales Co., Ltd..

HHS-2 electronic constant temperature water bath, Shanghai Kanglu Instrument Equipment Co., Ltd.; JJ-1 precision booster, Changzhou Boyuan Experimental Analytical Instrument Factory; Electronic balance, 2000g/0.01g, Shanghai Huachao Electric Co., Ltd.; Electric thermostat blast drying oven, Shanghai Jinghong Experimental Equipment Co., Ltd.; Infrared spectrometer, BRUKER VERTEX-70, Bruker, Germany; i-Strentek 1510 electronic universal testing machine, Jinan Blu-ray Electromechanical Technology Co., Ltd.; Scanning electron microscope, model FEG250, Beijing Oubo Tong Optical Technology Co., Ltd.; YS20B nickel-copper filter radiator, Taizhou Yishun Valve Co., Ltd.% Tianjin Zhiyuan Chemical Reagent Co., Ltd.
2.2. Slurry preparation
To prepare the chitosan solution, we mixed and stirred 8 g of NaOH, 4 g of urea and 88 g of water to obtain the chitosan dissolution system with 8% NaOH and 4% urea [17]. Then, the chitosan powder was dispersed into the mixture, which was stirred for 20 min to obtain a chitosan suspension. Then we chilled this suspension to -30°C and stirred it three times during this time. Finally, it was thawed at room temperature to obtain the transparent chitosan solution.

To prepare the gelatinized starch, we poured 100 g of distilled water and 24 g of starch into beakers. The mixture was then stirred. A uniform suspension of the starch was obtained, and the beakers were placed in a water bath at a constant temperature of 80°C. The contents were stirred using a blender for 30 min to obtain gelatinised starch.

2.3 Test concerning the effect of Slurry viscosity
(1) Experimental study on the effect of formulation concentration on slurry viscosity
Take five 500ml round bottom beakers, the prepared chitosan and starch slurry were mixed and disposed in 5 beakers in a ratio of 1:0, 1:0.5, 1:1, 1:1.5, and 1:2. Then set the precision magnetic stirrer rotation speed to 80r/min and stirred for 30 minutes, stood for 24 hours at room temperature. Then, the viscosity was measured by using a viscometer, and the shear rate of the rotor was set to 100 s⁻¹, with the slurry temperature was 20 ℃ at room temperature. The experimental data was collected every 0.2 seconds to record the stable viscosity data. Repeated the experiment five times and recorded the experimental data, then removed the collected data from the collected data points and drew the viscosity characteristic curve.

(2) Experimental study on the effect of Temperature on slurry viscosity
Take five 500ml round bottom beakers, the prepared chitosan and starch slurry were mixed and disposed in 5 beakers in a ratio of 1:1.5. Then set the precision magnetic stirrer rotation speed to 80r/min and stirred for 30 minutes, stood for 24 hours at room temperature. The five beakers were placed in a constant temperature water bath at a temperature of 20°C, 40°C, 60°C, 80°C, and 100°C. After one hour, the viscosity of the mixed slurry was measured at the corresponding temperature. The experimental data was collected every 0.2 seconds, to record the stable viscosity data. Repeated the experiment five times and recorded the experimental data, then removed the collected data from the collected data points and drew the viscosity characteristic curve.

(3) Experimental study on the effect of Single/integral plastic modification on slurry viscosity
100 g of starch slurry and 100 g of chitosan slurry were treated with glycerol 1.875 g, respectively. Took three 500ml round bottom beakers and mixed plasticized chitosan and common starch (PC-S), plasticized starch and common chitosan (PS-C), plasticized chitosan and plasticized starch (PCS) according to the ratio of starch: chitosan=1:1.5 (The above three kinds of slurries were simply referred to as "PC-S/PS-C/PCS" hereinafter), and then the above process was repeated for viscosity measurement.

2.4 FTIR test
The different plasticized mixed slurry was dried in a 100°C incubator for 24 h. 5g sample and 300mg KBr powder were mixed and fully ground to a particle diameter of less than 2.5. The ground mixture was transferred to a tableting mold and applied a pressure of about 12 to 14 MPa to a transparent or translucent sheet. Place the sheets on the holder of the infrared spectrometer separately and set the sampling frequency to 400-4000cm⁻¹. Then run the program to scan the sample, printed and saved the spectrum. Finally, we analyzed peak shape attribution.

2.5 XRD test
The remaining powder of the infrared spectrum test was taken 5 g, which was ground with an agate grinding dish until the particle size was 195 mesh. The test was carried out at room temperature by using a graphite curved crystal monochromator and a nickel copper filter radiator. During the sample test, the sample and the glass frame must be flush and the sample should be flat. The index of the seam
system was DS/RS/SS =1°/0.16 mm/1°. The test used Cu-Kα ray, Ni filter, the tube pressure was set to 35 KV, the tube flow was set to 25 mA sweep, the drawing speed was 5 (°)/min, the analysis angle (2θ) and the interval was 10-90°.

2.6. SEM test
All the samples were mounted on the aluminum short post with a ribbon, and a gold water coating was sputtered on the surface of the slurry to make it thermally conductive. Then the inside of the PC-S/PS-C/PCS mixed slurry was observed by using a scanning electron microscope. The electron microscope needed to have an accelerating voltage of 10 kv.

3. Experimental analysis

3.1 Effect of temperature on slurry viscosity
The rheology of a material was usually characterized by viscosity. The lower the viscosity of the material, the better its rheological properties. The viscosity test results of the mixed slurry at different temperatures were shown in Fig.1. The viscosity of the slurry decreased firstly and then increased with the increase of temperature. The viscosity of the slurry reached a minimum at 60℃ and was 10,425 cp. At the beginning, due to the rise of temperature, the thermal motion of the molecules inside the slurry was accelerated, the energy of the microscopic particles or groups in the slurry was increased, the binding force between the molecules was reduced, the mixed slurry was easily stirred, and the viscosity was reduced. When the temperature continued to rise to a certain critical value, the molecular thermal motion was too intense that the microscopic particles collided with each other, the energy was reduced, and the viscosity was reduced.

![Fig.1 Viscosity curve with temperature](image1)

![Fig.2 Viscosity curve with starch concentration](image2)

3.2 Effect of concentration on slurry viscosity
The results of slurry viscosity test when chitosan and starch were mixed according to different proportions were shown in Fig.2. The results showed that the viscosity of the mixed slurry decreased firstly and then increased with the increase of starch content. The viscosity of the slurry after mixing was reduced compared to the viscosity of the individual slurry. The chitosan molecule and the starch molecule were connected by hydrogen bonding as shown in Figure 4, starch and chitosan contained a large amount of hydroxyl groups. During the mixed process, the starch molecules and the chitosan molecules were connected by hydrogen bonds, resulted in a decrease in the binding force between the molecules [18]. The viscosity was reduced. Moreover, as the starch content was increased, agglomeration occurred between the starch molecules and the viscosity increased correspondingly.

3.3 Effect of Single/integral plastic modification on slurry viscosity
The results of viscosity test when plasticizing the mixed slurry of different modification methods showed that PS-C had the highest viscosity, PCS viscosity was the second, and PS-C had the lowest
viscosity. The results showed that the viscosity of the slurry would be greatly reduced when the slurry was plasticized. The viscosity of the co-plasticized slurry was reduced by 51.4% compared to the viscosity of the unplasticized slurry. It was concluded that the plasticizing treatment was beneficial to reduce the rheology of the slurry.

3.4. FTIR results

![FTIR spectra](image1)

**Fig. 3** The infrared spectra of PCS/PS-C/PC-S

In order to explain the change of the viscosity of the slurry from a microscopic point, the three kinds of slurries were tested by infrared spectroscopy. In this study, the O-H stretching vibration absorption peak in the FTIR spectrum was located at 3000-3600 cm⁻¹, and the lower the hydroxyl peak frequency, indicating the formation of new hydrogen bonds [19]. An intermolecular hydrogen bond shown in Fig. 3 was formed between chitosan and starch. Figure 5 showed the FTIR spectrum when plasticizing different components. The results showed that the hydroxyl absorption peak frequency of PS-C was the lowest, and the number of hydrogen bonds formed was the largest, which also led to the highest viscosity among the three treatment methods. Followed by PC-S, and finally PC-S. The FTIR test results showed that the order of the number of hydrogen bonds formed was the same as the order of the viscosity size of the slurry, which indicates that the formation of hydrogen bond would affect the rheology of the slurry, and the more the number of hydrogen bond formation was, the greater the viscosity of the slurry.

3.5 XRD results

In order to further verify the results of the FTIR test, XRD was tested on both PC-S and PCS slurries. The test results were shown in Fig. 4. The results showed that PC-S had a peak at 2θ=20.96°, 30.98°, whereas PCS had a peak at 2θ=21.04°, 31.02°. The peak intervals of the two were similar, which indicated that PC-S and PCS had similar crystal microscopic morphology. The crystallinity of a material was usually characterized by a crystallinity index, and the greater the crystallinity index of the material, the higher its crystallinity. The processing and analysis by Jade software showed that the crystallinity index of PCS was significantly smaller than that of PC-S, which indicated that the crystallinity of PCS was reduced when it was modified. Polymer materials such as starch and chitosan were composed of a crystalline region and an amorphous region. The degree of crystallinity was used to some extent to indicate the size of the crystalline region. The lower the crystallinity, the smaller the crystalline region of the material, the larger the amorphous region, and the more the free branch in the amorphous region, which was more conducive to the combination between starch and chitosan. So the combination between the two was closer, which resulted in a higher viscosity.

3.6 SEM result

To further explain the correctness of FTIR and XRD, SEM analysis was performed on the three mixed slurries. The results were shown in Fig. 5, in which Fig. (a) was a PS-C structure diagram, Fig. (b) was a P slurry structure diagram, and Fig. (c) was a slurry structure diagram of PCS. The internal structure...
of PS-C was a block structure with tight bonding, few pores, and the highest viscosity of the slurry; The internal structure of PC-S was a network structure with many pores and low viscosity; When chitosan and starch were co-plasticized, the structure of the slurry was a reticulated joint block structure. The void was less than PC-S, so its viscosity was greater than the viscosity of PCS.

4. Conclusions
The viscosity of the chitosan/starch film mixed slurry decreases at first and then increases with the increase of temperature and starch content, the viscosity reaches the lowest at 60 °C and at the chitosan: starch=1:1.5. Effect of single/integral plasticization modification on slurry viscosity: PS-C>PCS>PC-S. The FTIR test of the single/integrated plasticized slurry shows that the hydroxyl absorption peak of PS-C is closer to the low frequency, then the PCS, and finally the PC-S. The amount of hydrogen bonds formed is related to the rheology of the slurry. The XRD test results shows that the crystallinity of PS-C is significantly smaller than that of PCS, which makes it less rheological. SEM test results shows that the internal structure of PS-C is a block structure with tight bonding and few pores; The internal structure of PC-S is a network structure with many pores; When chitosan and starch were co-plasticized, a sheet-like structure is formed on a large area, and a network structure is generated between the sheets.

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