



Cross-linked modification of tapioca starch by sodium Trimetaphosphate: An influence on its structure

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ABSTRACT

This study aimed to examine the changes in the structural characterization of cross-linked tapioca treated with sodium trimetaphosphate (STMP). The degree of substitution in the cross-linked starch was determined by the iodine absorption method. Scanning electron microscopy, particle size measurement, Fourier-transform infrared spectroscopy (FT-IR), and x-ray diffraction (XRD) were used to characterize the structure of modified tapioca starch at different substitution degrees. The results demonstrated that the degree of substitution of cross-linked starch increased with the increase in the amount of the cross-linking agent. The modified starch particles aggregated to form a mass structure, but the average particle size did not change with the cross-linker content and was about 17 μm . FT-IR and XRD experiments showed that the cross-linking esterification of starch with sodium trimetaphosphate generated new phosphate groups, increasing the content of phosphoric acid in starch, and the A-type crystalline structure of starch was not changed.

1. Introduction

Starch is abundant in nature, usually in the form of semi-crystalline insoluble particles within the plastids of leaves, seeds, and storage organs (Seung, 2020). It is derived from grains, tubers, roots, beans, and some unripe fruits. Starches is a polysaccharide consisting of repeated glucose units linked by glycosidic bonds (Khurshida et al., 2021). They have two main components: amylose and amylopectin. Amylopectin (AP) is a 1,4-A-D glucan with a high density of branched chains, linked by α -1, 4 and α -1, 6-glucoside bonds. Amylose (AM) is a relatively linear 1,4-A-D glucan with a small number of branches connected by α -1,4-glucoside bonds (Zhu et al., 2017). The amylopectin content accounted for 70%–80% and the amylose content accounted for <30% of the starch composition (Dimantov et al., 2004). Starch particles, consisting of alternating layers of amorphous and crystalline flakes (100 nm and 400 nm thick), exhibit a variety of shapes. These can range from smooth spherical and elliptical forms to rather irregular polygons. The crystal flakes of starch particles are composed of double spiral amylopectin side chain clusters, whereas the amorphous flakes are composed of amylopectin branch chains and amylose chains (Amaraweera et al., 2021).

Starch is a cost-effective, readily available, nontoxic, and renewable

resource, making it invaluable in industries such as paper, food, packaging, textiles, biofuels, and others (Liu, 2023). Among various starch sources, tapioca is one of the high-yield sources, mainly grown in tropical and subtropical regions and is an essential tropical food crop after rice and maize in terms of yield (Zhu, 2015). Natural tapioca starch has excellent paste viscosity, paste clarity, freeze–thaw stability, and other remarkable characteristics and is an excellent biological raw material (Jyothi et al., 2006). In the food industry, tapioca starch is known for its light and sweet taste, making it popular among customers. In the nonfood industry, tapioca starch can be used as a bio-based material to make degradable films, for ethanol production, and so on.

However, natural starch has certain limitations such as high-temperature resistance, low shear resistance, and high recovery trend. Also, it does not have the ideal performance for specialized applications, limiting the use of starch in some industries (Liu, 2023; Singh et al., 2007). Therefore, natural starch can be modified by physical, chemical, and enzymatic methods to improve the functional properties of starch. Physical modifications primarily include hot and wet treatment, gelatinization and rejuvenation, hydrothermal annealing, ultrasonic treatment (Thakur et al., 2021), ball milling or grinding, high-static pressure water, and so forth (Wang et al., 2023). For enzymatic modifications, the

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Table 1
Substitution degree of cross-linked tapioca starch.

Sample name	Absorbance	Light transmittance (%)	Degree of cross-linking (%)
TS	0.3650	43.18	0
0.5% STMP-CL-TS	0.2540	55.73	30.50
1% STMP-CL-TS	0.2167	60.60	40.73
1.5% STMP-CL-TS	0.1933	63.14	47.22
2% STMP-CL-TS	0.180	66.40	50.96
2.5% STMP-CL-TS	0.1576	69.91	57.63
3% STMP-CL-TS	0.1397	72.57	61.74

enzymes used are mainly divided into glycosyl hydrolase and transglycosylation enzymes (Punia Bangar et al., 2022), such as debranchase (Pullulanase), α -amylase, β -amylase, cyclodextrin glycosyltransferase, and so on (Liu et al., 2022). Chemical modification is the most prevalent and widely used method for starch modification. The specific chemical modification technique chosen depends on the starch source, reaction conditions (concentration, reaction time, pH value, the presence of the catalyst, and the type of substituent), degree of substitution, and other physical and chemical conditions. Different physicochemical conditions make the types of chemical modifications different (Chen et al., 2015). Modifying natural starch particles profoundly alters its gelatinization, rejuvenation, viscosity, and other properties (Ashogbon & Akintayo, 2014), thereby improving the performance of starch. Chemical modification methods are mainly divided into cross-linking, oxidation, grafting, esterification, acid hydrolysis, etherification, and so on.

Cross-linking is one of the most commonly used chemical modification methods. Cross-linked starch results from the formation of ether or ester bonds between hydroxyl groups of natural starch under the action of the cross-linking reagent (Guo et al., 2015). Because cross-linking strengthens the hydrogen bonds in starch, it enhances the gelatinization temperature, shear stability, resistance to acidic pH, mechanical properties, and water resistance of starch (Gao et al., 2014; Guo et al., 2015). However, most cross-linkers are expensive, toxic, or inefficient (Tanerungroj & Prachayawarakorn, 2018). On the contrary, sodium trimetaphosphate (STMP) is a green, nontoxic, inexpensive, mild, and controllable cross-linking reagent (Li et al., 2009). Sodium trimetaphosphate is a cyclic triphosphate obtained from the condensation of phosphate (P) and pyrophosphate (PP) at high temperatures. Starch phosphate prepared from sodium trimetaphosphate is a distarch phosphate (under alkaline conditions), with good freezing resistance and thawing properties (Sang et al., 2010). Given environmental and safety issues, sodium trimetaphosphate (STMP) was used to cross-link tapioca starch in this study.

In this study, tapioca starch was used as a raw material, and the degree of substitution of cross-linked tapioca starch was determined by the iodine absorption method, which was accurate and fast. The normal blue complex formed between starch and iodine was used to determine the amount of cross-linked starch (Xing et al., 2016). The degree of substitution of the modified starch was used as an index to compare natural starch. Subsequently, the particle morphology and particle size distribution of starches with varying cross-linking degrees were detected using scanning electron microscopy and laser particle size distribution. At the same time, the molecular structure and crystal morphology of cross-linked starch were studied by Fourier infrared spectroscopy (FT-IR) and x-ray diffraction (XRD). The main purpose of this study was to determine whether the structure of the starch after cross-linking was changed using sodium trimetaphosphates. This study aimed to enhance our understanding of cross-linked starch and provide a theoretical basis for the subsequent preparation of excellent modified tapioca starch and bio-based films related to modified starch.

2. Materials and methods

2.1. Materials

Commercial natural tapioca starch (origin from Jiaying, Zhejiang Province, China) was purchased from Fengwei Industrial Limited Company (Shanghai, China), and sodium trimetaphosphate from Pitt Medical Technology Corporation Limited Company (Shanghai, China). I_2 , KI, and silver nitrate agents were purchased from McLean Biochemical Technology Corporation Limited Company (Shanghai, China). Anhydrous ethanol (ethanol content $\geq 99.7\%$) was purchased from Xilong Science Limited Company (China). All chemicals used to prepare and analyze starch were analytical reagent grade.

2.2. Preparation of cross-linked tapioca starch

An appropriate amount of starch was weighed and added to distilled water to prepare natural tapioca starch slurry, which was titrated with 0.1 mol/L NaOH solution to pH 11.0. The content of sodium trimetaphosphate was added to 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, and 3.0% (based on the dry weight of starch), and three parallel sets were used in each group on average. After stirring with a magnetic stirrer (MS-H-Pro⁺, Dalong, Beijing, China) for 15 min, the starch slurry was placed in a constant-temperature water bath (HH-4, Aohua Limited Company, Changzhou, Zhejiang Province, China) at 50 °C for 3.5 h. After the reaction, the pH of the starch slurry was adjusted to neutral using 0.5 mol/L hydrochloric acid. The slurry was then centrifuged using a refrigerated high-speed centrifuge (Centrifuge 5804 R, Eppendorf Aktiengesellschaft, Germany) at 10,000 rpm for 15 min. After centrifugation, the slurry was washed with anhydrous ethanol several times, until no color change was observed upon adding silver nitrate solution to the filtrate. Finally, the samples were dried in an oven at 50 °C for 11 h and then sifted with a 100-mesh sieve to obtain the final samples (Wongsagonsup et al., 2014; Pradyawong, Juneja, Sadiq, Noomhorm and Singh, 2018).

2.3. Determination of the substitution degree of cross-linked starch

The iodine absorption method was used to measure the degree of substitution of cross-linked tapioca. First, the I_2 -KI solution was prepared and stored in a 100-mL brown bottle. A blank control group was established, along with six groups of cross-linked starch with different concentrations of sodium trimetaphosphate. Three parallel sets were set up for each group. Each 0.1 g sample was weighed and placed in a 15-mL centrifuge tube. Further, 1 mL of ethanol was added and the mixture was agitated using a vortex mixer (XW-80 A, Qingpu Luxi Instrument Factory, Shanghai, China). At the same time, 9 mL of 0.1 mol/L NaOH solution was added. This solution was then transferred to a 100-mL volumetric flask, the volume was set to 100 mL, and mixed well. Next, 5 mL of the aforementioned solution was transferred to another 100-mL volumetric flask. To this flask, 3 mL of 1 mol/L hydrochloric acid was added and then 1 mL of I_2 -KI solution was added to discolor the solution (Avaro et al., n.d.). Further, deionized water was added, and the volume was set to 100 mL. The absorbance values of raw starch and cross-linked starch were measured at 720 nm using a double-beam UV-vis spectrophotometer (L8, Yidian Analytical Instrument Limited Company, Shanghai, China). The cross-linking degree (CL%) was calculated as follows (Kou & Gao, 2018):

$$CL\% = (A-a)/A \times 100$$

where A is the absorbance value of natural starch, and a is the absorbance value of cross-linked starch.

2.4. Particle surface analysis

The samples were observed using a particle surface analysis system

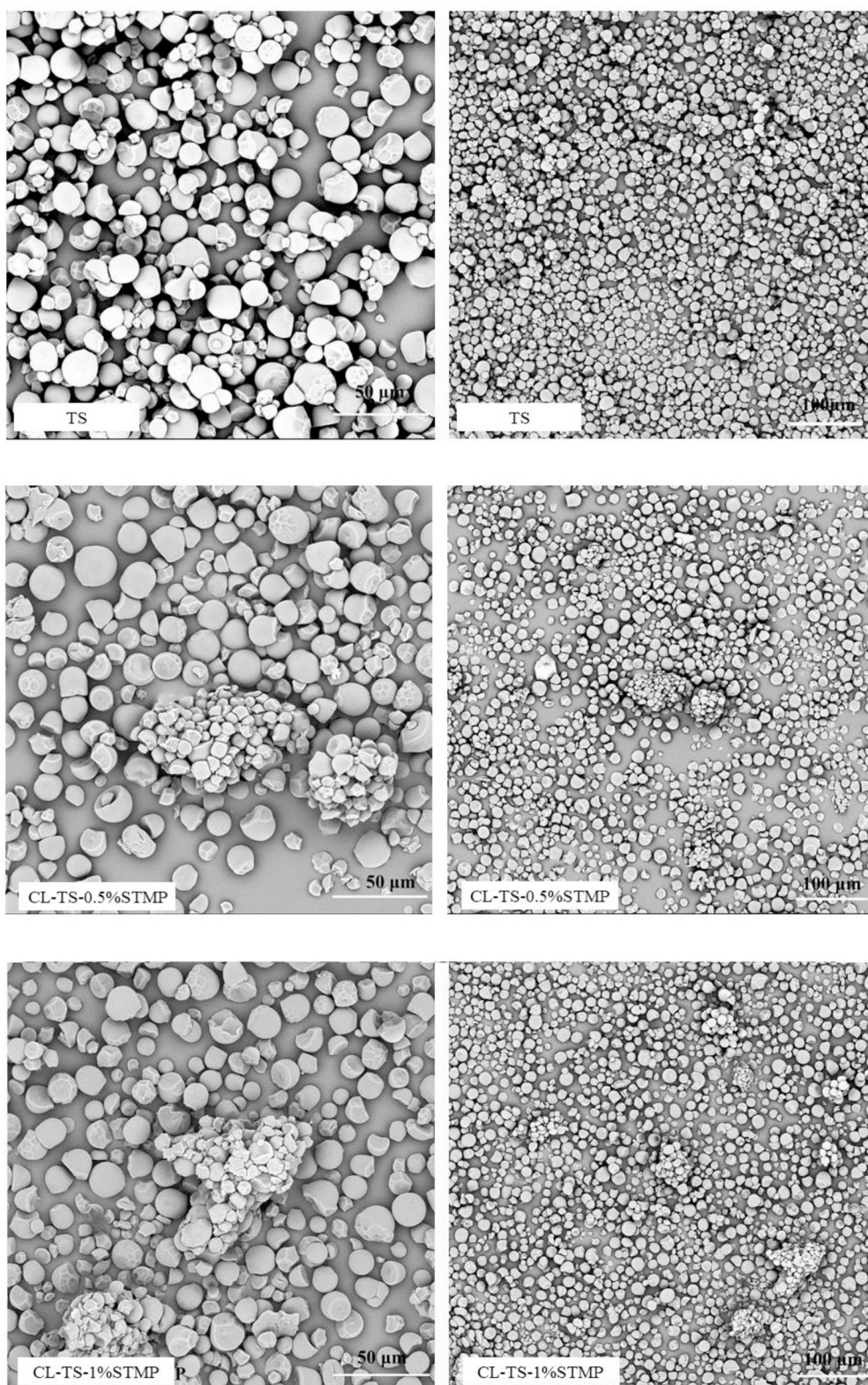


Fig. 1. Particle morphology of tapioca starch after cross-linking with different concentrations of STMP. The scanning electron microscope (SEM) image on the left is 50 μm in scale, and the SEM image on the right is 100 μm in scale.

Note: TS is natural tapioca starch.

CL-TS-0.5%STMP is tapioca starch cross-linked with 0.5% STMP.

CL-TS-1%STMP is tapioca starch cross-linked with 1% STMP.

CL-TS-1.5%STMP is tapioca starch cross-linked with 1.5% STMP.

CL-TS-2%STMP is tapioca starch cross-linked with 2% STMP.

CL-TS-2.5%STMP is tapioca starch cross-linked with 2.5% STMP.

CL-TS-3%STMP is tapioca starch cross-linked with 3% STMP.

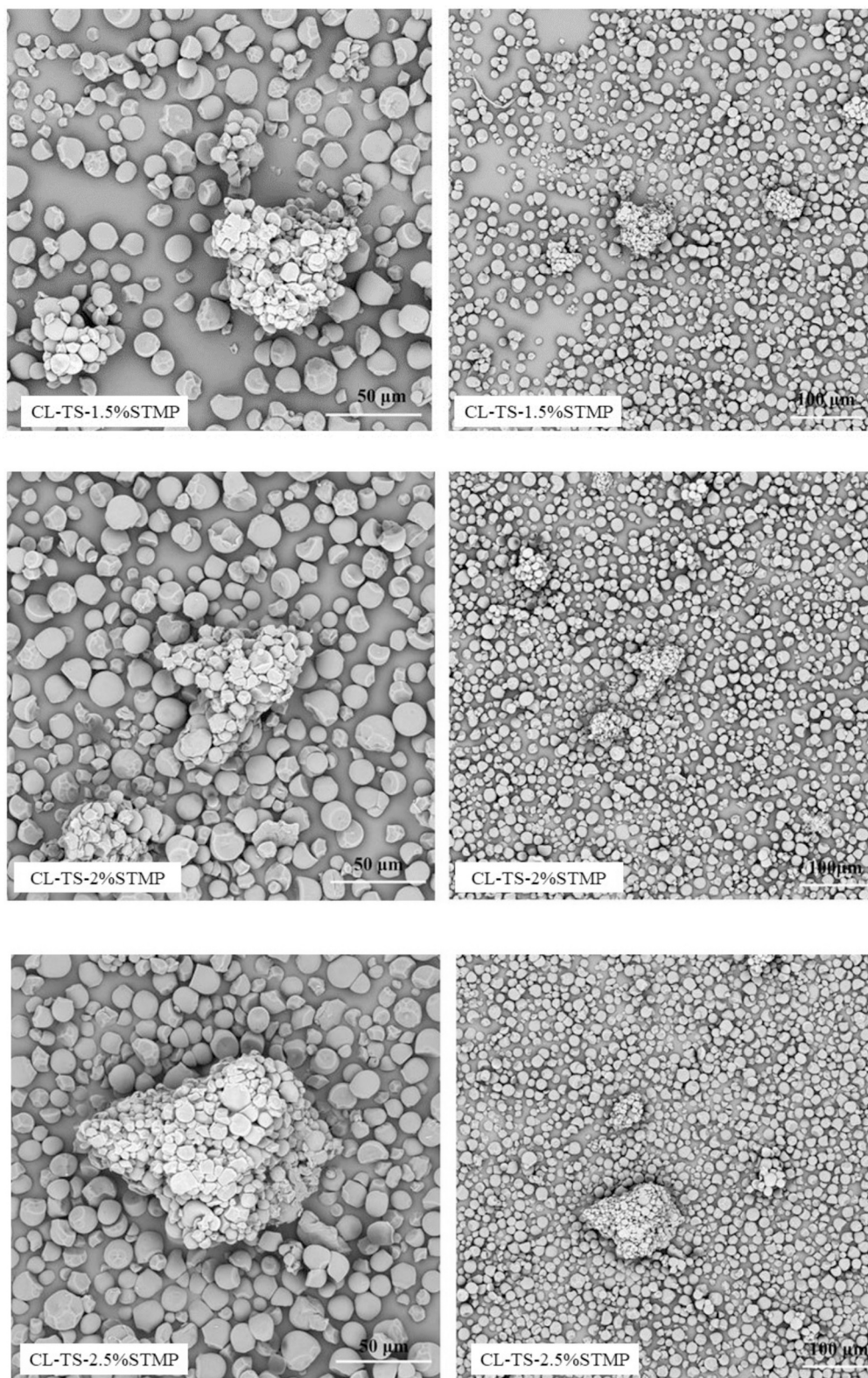


Fig. 1. (continued).

(scanning electron microscopy) (Phenom-World BV, Netherlands). After the sample was carefully ground, double-sided tape was affixed to an aluminum post. Starch particles were then applied evenly to the tape. They were subsequently sprayed with gold. The sample was observed and photographed at an accelerated voltage of 10 kV (Zhou et al., 2014).

2.5. Particle size measurement

The particle size of seven natural and cross-linked tapioca starch samples was measured using a laser particle size distribution instrument (BT-9300S, Danton Baxter Limited Instrument Company, Liaoning, China), and each sample was measured three times in parallel.

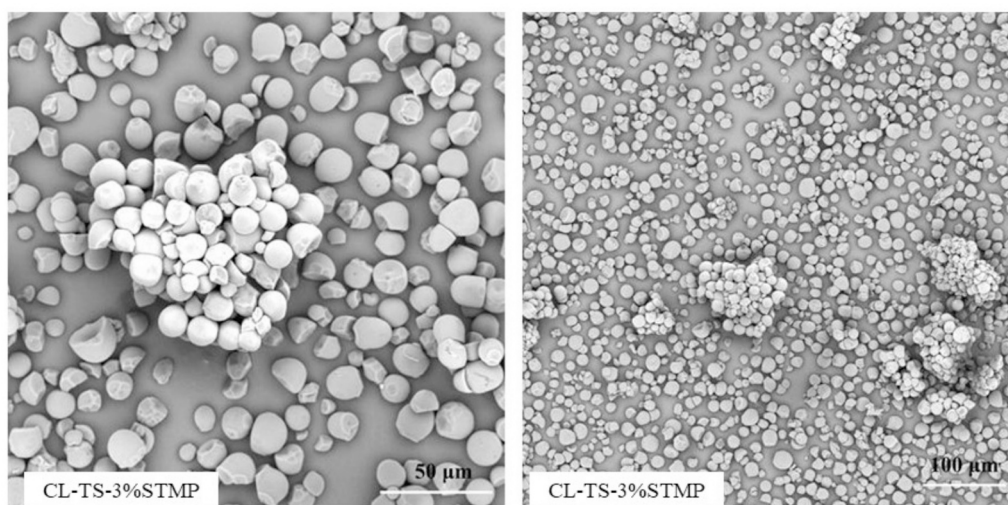


Fig. 1. (continued).

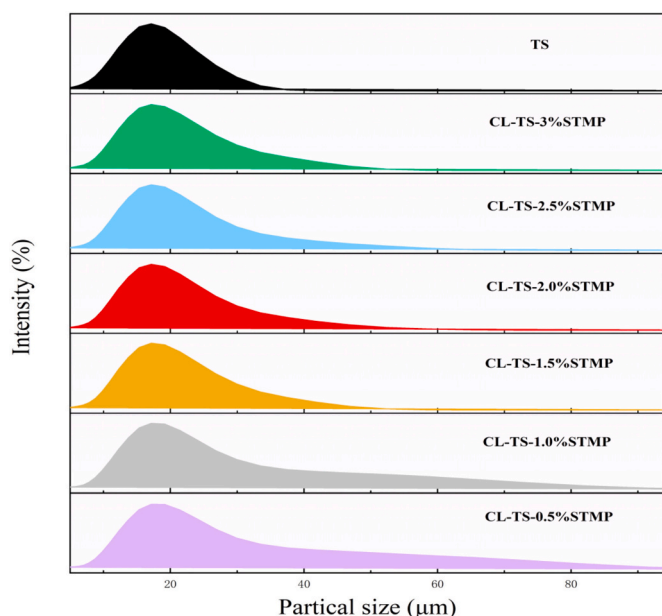


Fig. 2. Particle size distribution of tapioca starch after cross-linking with different concentrations of STMP.

Note: TS is natural tapioca starch.

CL-TS-0.5%STMP is tapioca starch cross-linked with 0.5% STMP.

CL-TS-1%STMP is tapioca starch cross-linked with 1% STMP.

CL-TS-1.5%STMP is tapioca starch cross-linked with 1.5% STMP.

CL-TS-2%STMP is tapioca starch cross-linked with 2% STMP.

CL-TS-2.5%STMP is tapioca starch cross-linked with 2.5% STMP.

CL-TS-3%STMP is tapioca starch cross-linked with 3% STMP.

2.6. Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FT-IR) (T27, Bruker Company, Germany) of the sample was performed using a Fourier-transform infrared spectrophotometer. The samples were mixed with KBr under anhydrous conditions and infrared irradiation and recorded in the wavenumber range of 400 to 4000 cm^{-1} (Heo et al., 2017).

2.7. XRD measurement

X-ray diffractometry (Smart Lab, Rigaku, Japan) was used to analyze

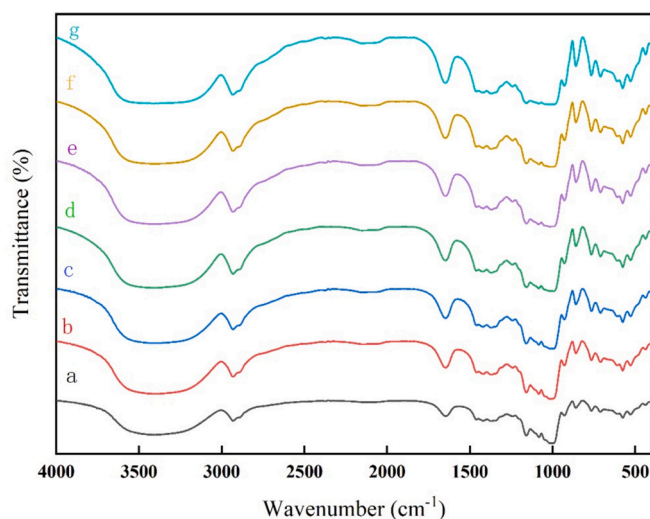


Fig. 3. (a) Fourier-transform infrared spectrum of natural tapioca starch. (b) Fourier-transform infrared spectroscopy of tapioca starch cross-linked with 0.5% STMP. (c) Fourier-transform infrared spectroscopy of tapioca starch cross-linked with 1.0% STMP. (d) Fourier-transform infrared spectroscopy of tapioca starch cross-linked with 1.5% STMP. (e) Fourier-transform infrared spectroscopy of tapioca starch cross-linked with 2.0% STMP. (f) Fourier-transform infrared spectroscopy of tapioca starch cross-linked with 2.5% STMP. (g) Fourier-transform infrared spectroscopy of tapioca starch cross-linked with 3.0% STMP.

the XRD pattern, and the relative crystallinity of the starch was determined at 40 kV, 100 mA, and an angle range of 2θ , from 5° to 40° (Ma et al., 2022).

3. Discussion and analysis

3.1. Substitution degree of cross-linked starch

The cross-linking degree of modified starch was determined by the blue complex formed normally between amylopectin and iodine in a left-hand spiral, with six residues per turn (Rundle & Baldwin, 1943). Under appropriate conditions, cross-linking occurred between amylopectin molecules or within a single amylopectin molecule after the addition of the cross-linking agent STMP. The hydroxyl groups on the

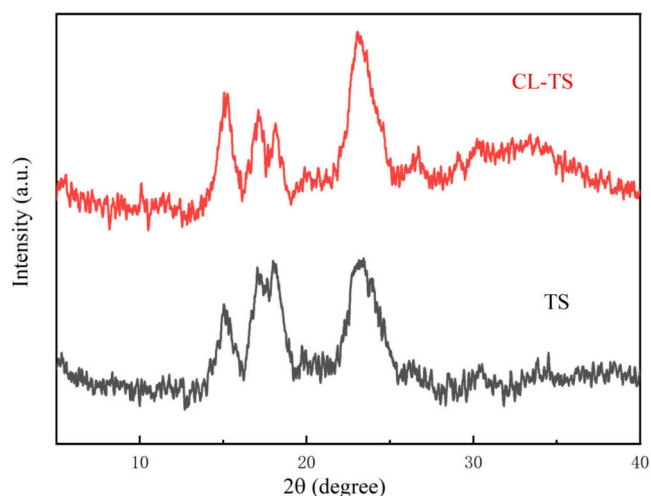


Fig. 4. X-ray diffraction patterns of natural tapioca starch and cross-linked tapioca starch.

Note: TS is natural tapioca starch.

CL-TS-STMP is tapioca starch cross-linked with STMP.

starch were continuously replaced by phosphate groups, and phosphodiester bonds were formed. The amylose molecules usually do not cross-link with each other. However, the cross-linking between amylose and amylopectin increased with the increase in the amount of the cross-linking agent. The new structure formed by the interaction between amylopectin molecules was recognized as amylopectin, resulting in a decrease in the perceived amylose content. (Kou & Gao, 2018; Zhang et al., 2013). Therefore, the decrease in amylose content led to a decrease in amylose–iodine blue-green complex content, subsequently reducing the light absorption value and increasing the substitution degree. In this experiment, the natural tapioca starch (TS) was compared with cross-linked tapioca starch (CL-TS) containing varying amounts of sodium trimetaphosphate (STMP). The content of sodium trimetaphosphate ranged from 1% to 3% (based on starch dry weight), the blue-green color in the sample solution gradually became lighter, the absorbance value gradually decreased. Table 1 shows the increase in cross-linking degree from 30.50% to 61.74%, accompanied by a gradual rise in the degree of substitution.

3.2. Particle morphology analysis

As illustrated in Fig. 1, the natural tapioca starch particles had round, oval, and irregular shapes, with clear edges and partial pits on some particles. Some of the starch preparation processes, such as heat treatment, grinding, or extrusion, caused the particles to break slightly (Hu et al., 2020). Compared with natural tapioca starch, the surface smoothness of some starch particles was lost, the edges were blurred, and the particles interacted with each other due to the destruction of the ordered crystal structure of some starch particles after the cross-linking reaction (Xie & Shao, 2009), thus leading to the binding and aggregation of particles. Large molecular particles of cross-linked starch attracted small molecular particles of cross-linked starch to form irregular clumps. The higher the level of cross-linking, the greater the interaction between particles, and the larger and more the starch granules formed.

3.3. Particle size analysis

The size of starch particles directly affects the crystalline properties of starch and the modification effect. The results of laser particle size distribution demonstrated in Fig. 2 that all samples had a principal particle size peak, indicating that most particle sizes were uniform. The average particle size of natural starch was 16.06 μm , whereas the

particle size of cross-linked starch slightly increased compared with that of natural starch. However, the change was not obvious, and the average particle size was about 17 μm . This might be because the cross-linked starch was slightly swollen in water. Consistent with the conclusion of Wang's study (Wang et al., 2018), the particle size change of tapioca starch could be negligible after cross-linking under the action of sodium trimetaphosphate and the average particle size was also about 17 μm . No significant correlation was found between the content of sodium trimetaphosphate and the grain size of tapioca starch.

3.4. Fourier-transform infrared spectral analysis

As shown in Fig. 3, the wide absorption peak at 3407 cm^{-1} was due to the overlapping of the absorption peaks attributed to multiple O–H stretching vibrations. The absorption peak at 2925 cm^{-1} corresponded to the asymmetric C–H tensile vibration of H–C–H (Hedayati et al., 2020). The absorption peak at 1649 cm^{-1} was caused by the tensile vibration of O–H. In the 1330–400 cm^{-1} fingerprint region, the group absorption peak of the cross-linked starch was the same as that of natural starch. The absence of a characteristic absorption peak indicated that the original structure of starch was not changed by cross-linking esterification. As stated in the study by Sitohy and Pérez (Pérez & Bertoft, 2010; Sitohy et al., 2000), phosphate ester groups were found in the original natural starch amylopectin. However, 887 cm^{-1} is the useful band for identifying phosphate groups (Ren et al., 2016). The number of phosphate groups in starch increased with the increase in the degree of starch cross-linking, leading to an increase in the absorption peak intensity in this region. Hence, it was concluded that STMP treatment led to increased phosphorus content in tapioca starch and successful phosphorylation of starch.

3.5. XRD analysis

As illustrated in the Fig. 4, natural tapioca starch displayed diffraction peaks at $2\theta = 15^\circ, 17^\circ, 18^\circ,$ and 23° , which proved that tapioca starch possessed an A-type crystal structure. For the cross-linked tapioca starch, the positions of the diffraction peaks remained the same, and the diffraction angle was $15.24^\circ, 17.12^\circ, 18.16^\circ,$ and 23.24° . The crystal structure of the modified starch was an A-type crystal structure. The crystalline and amorphous starch particles corresponded to the peak and dispersion area of the curve, respectively (Hu et al., 2014). This indicated that the ordered structure of starch particles did not change, and cross-linking occurred in the amorphous region of starch particles (Cao et al., 2022). Some of the diffraction peaks were slightly weakened, possibly because some hydroxyl groups were replaced by phosphate groups (Xie et al., 2022). The peaks weakened by 17.12° and 18.16° . The cross-linking agent destroyed the amorphous region and did not change the crystalline pattern.

4. Conclusions

This study explored the structural characterization of tapioca starch with varying substitution degrees cross-linked with sodium trimetaphosphate. The results indicated that the number of starch clumps formed by the aggregation of starch particles increased with the increase in the degree of cross-linked substitution. Large molecular particles attracted small molecular particles, thus resulting in a cluster structure. No characteristic absorption peak was observed in FT-IR spectroscopy, indicating that the original structure of tapioca starch was not altered by sodium trimetaphosphate. However, the characteristic peak strength of 887 cm^{-1} increased with the increase in the degree of cross-linked starch replacement because the phosphate groups in modified starch increased under the treatment of the cross-linking agent. The particle size of cross-linked tapioca remained relatively consistent, indicating that the content of the cross-linking agent did not change the particle size of starch particles, maintaining an average particle size of about 17 μm . At the

same time, XRD results confirmed that the crystal structure of cross-linked tapioca starch remained type A. The results of this study might provide some theoretical support for further modifications and research on tapioca starch. Based on its properties, cross-linked starch has been applied to textile research, papermaking, and preparation of functional packaging films.

CRedit authorship contribution statement

Zhijing Zheng: Validation. **Ying Zhao:** Conceptualization. **Jian Chen:** Writing – review & editing. **Shuai Tang:** Methodology.

Declaration of competing interest

The authors declare that there are no conflicts of interest in this research article.

Data availability

No data was used for the research described in the article.

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