Influence of electrolytes and hydroxypropylsulfonation on paste stability of cassava starch/polyvinyl alcohol blend sizes for warp sizing

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Abstract
The aim of this research was to ascertain the influences of electrolytes and hydroxypropylsulfonation on paste stabilities of cassava starch/polyvinyl alcohol blend sizes. The hydroxypropylsulfonated cassava starch was prepared via hydroxypropylsulfonation of hydrolyzed cassava starch with 3-chloro-2-hydroxypropyl sulfonic acid sodium in an aqueous medium. The stability was evaluated by measuring the initial demixing time. Before and after the addition of the electrolytes such as NaH₂PO₄, Na₂SO₄, and NaCl, the initial demixing time was 24, 20, 18, and 15 min for hydroxypropylsulfonated cassava starch/PVA1799 paste and 21, 17, 15, and 14 min for hydrolyzed cassava starch/PVA1799 one. This showed that the electrolytes accelerated the separation rates of hydroxypropylsulfonated cassava starch/polyvinyl alcohol blend pastes and hydrolyzed cassava starch/polyvinyl alcohol ones, thereby reducing the stability, and the acceleration followed the order: NaH₂PO₄ > Na₂SO₄ > NaCl. Increasing the concentration of electrolyte accelerated the separation rate and lowered the stability. The hydroxypropylsulfonation was able to reduce the separation rate and enhance paste stability. When the weight percentage of starch was fixed, with the rise in the degree of substitution from 0.011 to 0.029, the initial demixing time gradually increased, indicating the gradual decreases in the separation rates, thereby promoting the enhancement in the stability. Moreover, PVA0588 was lower than PVA1799 and PVA1788 in affecting the separation rate, which implied that polyvinyl alcohol with a lower degree of polymerization favored to promote the stability.

Keywords
Hydrolyzed cassava starch, hydroxypropylsulfonation, PVA, phase separation rate, stability

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Introduction
Starch, due to its low cost,¹,² renewability,³ biodegradability, and so forth, has been widely adopted in textile sizing and paper making as a sizing agent.⁴,⁵ Polyvinyl alcohol (PVA) is also very useful in textile industry as a sizing agent.⁶ Starch and PVA are usually used in a form of blended paste for sizing cellulose/synthetic blend spun yarns.⁷ However, the hydroxyl groups in starch molecules tend to associate with each other, and the same is the hydroxyls in PVA molecules. This will lead to a lower association between the hydroxyls in the starch and PVA molecules. Therefore, due to thermodynamical incompatibility between starch and PVA, the starch/PVA blend paste commonly produces phase separation behavior during the time period of the paste applied for sizing.⁸ In addition, in dilute starch and PVA...
blend paste, due to the regular arrangement of amyllose molecular chains arisen from the hydrogen bonding, it will form the macromolecular aggregates. With the increase in the volume of the aggregates, it can happen in the macroscopic phase separation phenomenon, producing the subsidence. The subsidence can lead to the instability of the paste. The instability is able to cause a decrease in size add-on, which can adversely affect the adhesion of the paste to fibers and the integrity of film formed around the surfaces of warps, thereby leading to a reduced weaving efficiency. Therefore, it is an urgent demand to reduce phase separation rate of starch/PVA blend paste, so as to improve the stability of the blend paste.

Apparently, it is objective for electrolytes to exist in industrial raw starch and modified starch. Soaking process in wet process of starch production, acid-base neutralization, starch phosphate esterification, and so on are the main processes of producing the electrolytes. If these starches are not thoroughly washed in subsequent processes, the products will inevitably contain the corresponding electrolytes, such as NaCl, Na2SO4, and NaH2PO4. These inorganic electrolytes affects the stability of starch/PVA blend paste, and therefore, the influence shall be investigated in this work by accessed the separation rate.

In this work, we attempted to improve the stability by reducing the initial phase separation rate through performing chemical hydroxypropylsulfonation to cassava starch. The hydroxypropylsulfonation of cassava starch was performed by reacting hydrolyzed cassava starch (HS) with 3-chloro-2-hydroxy-1-propanesulfonic acid sodium salt (CHPS-Na) in aqueous medium, as shown in Figure 1. The hydroxypropylsulfonate (HPS) substituents derivatized on the backbone of starch are capable of exhibiting the strong steric restriction. Obviously, the restriction of the substituents favors to obstruct the re-association of starch hydroxyls and the regular arrangement of starch amylloses in the paste, thereby helping to reduce the aggregation speed of starch macromolecules. As a result, blending hydroxypropylsulfonated cassava starch (HPSS) with PVA can be expected to alleviate subsidence rates of aggregates and swollen fragments of starch, improving the stability of starch/PVA blend paste. For the reason, HPSS was prepared and adopted to investigate its influence on the separation rate.

However, when there is the electrolyte in the blend paste, its influence on the separation rates of HS/PVA and HPSS/PVA blend pastes has not been ascertained. In addition, there was no research about the influence of the hydroxypropylsulfonation on the separation rate at the existence of the electrolyte. Therefore, the aim of this work was to determine the influence of the electrolyte (such as its type and concentration) on the separation rates of HS/PVA and HPSS/PVA blend pastes, and reveal if the hydroxypropylsulfonation can reduce the separation rate. Moreover, the influence of degree of substitution (DS) on the separation rate was also investigated since the usability of a modified starch depends on the DS. And weight percentage of starch sample, degree of polymerization, and degree of alcoholysis of PVA were also estimated for exploring their influences on the separation rates.

Materials and methods

Materials

Raw cassava starch was purchased from Senhang Industrial Co. Ltd. (Shanghai, China). The 3-chloro-2-hydroxy-1-propanesulfonic acid sodium salt (CHPS-Na) was obtained by Jiaxing Sicheng Chemical Co. Ltd. (Zhejiang Province, China). All other chemicals such as NaH2PO4, Na2SO4, NaCl, HCl, NaOH, and so on were bought from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). PVA1799, PVA0588, and PVA1788 were supplied by Sinopec Sichuan Vinylon Works (Sichuan, China).

Modification of starch

Before the preparation of HPSS, HS was first prepared by reacting raw starch with HCl following a procedure described in the literature for reducing its excessive apparent viscosity.

The preparation of HPSS was carried out by the reaction of HS with CHPS-Na in an aqueous medium as shown in Figure 1. Briefly, a 40 wt% starch aqueous suspension was prepared by suspending 300 g of dried HS in distilled water (containing 30 g of Na2SO4). Afterward, the suspension was transferred into a flask and adjusted to pH 10–11 using a 3 wt% NaOH solution. Then, the suspension was stirred and heated to 45 °C in a water bath, and an aqueous solution of the CHPS-Na was added immediately. Thereafter, the suspension was adjusted to pH 11.5–12.5 and maintained for 7 h at 45 °C under mechanical stirring. Subsequently, the pH of the suspension was neutralized to approximately 7 with a dilute HCl solution, and vacuum-filtered. The rough product was washed with distill water for 3 times, dried in an oven (50 °C), pulverized, and sieved with a 100-mesh sieve to obtain the HPSS samples.

Characterization of starch

DS can be described as the average number of hydroxyls substituted per anhydroglucose unit. The DS was used
to indicate the numbers of HPS substituents introduced onto the starch chains in this work and was obtained by the calculation (based on the sulfur content from titration analysis)\textsuperscript{19} with the following equation (1)

\[
DS_h = \frac{162.5}{3200 - 138S}
\]

where \(S(\%)\) and 138 denote the sulfur content and molecular weight of \(-\text{CH}_2\text{CH(OH)CH}_2\text{SO}_3\text{H}\) minus that of hydrogen atom, respectively.

The surface morphology of the HS and HPSS granules was characterized with a S-4800 scanning electron microscope (Hitachi Limited, Japan). The granules were sputter-coated directly with a thin layer of gold before imaging.\textsuperscript{20}

**Preparation of the blend pastes**

Cooked starch aqueous pastes and PVA aqueous ones were prepared, respectively, followed by blending with different ratios for forming the blend pastes. First, a 3 wt\% of starch or PVA aqueous dispersion was prepared and transferred into a 3-necked flask. The dispersion was stirred and completely gelatinized at 95°C in a water bath. The gelatinized starch and PVA pastes were blended for 5 min at 90°C under thermostatic magnetic stirring. Then, 20 mL of the blend paste was immediately added into a test tube while the ground-glass stopper was covered. The tube was placed vertically at room temperature for observation. In addition, the corresponding electrolytes were added before starch gelatinization or after PVA dissolution.

**Measurement of phase separation behaviors**

Phase separation rate was evaluated in terms of initial demixing time (ID\(_t\)).\textsuperscript{8} The ID\(_t\) can be described as the time period from the addition of the paste into the tube to the occurrence of phase separation during observation. Two period results were recorded for each blend paste, and the average value was reported.

**Results and discussion**

**Characterization**

In this article, as shown in Figure 2, the granular HPSS samples prepared had the DS\(_h\) values of 0.011, 0.022, and 0.029, corresponding to the amounts of 10 g, 20 g, and 30 g of CHPS-Na to HS, respectively. The results of the DS\(_h\) values indicated that the DS\(_h\) of HPSS increased as the amount of CHPS-Na to HS raised, and also demonstrated that HPSS samples had been successfully synthesized. Furthermore, the successful introduction of HPS substituents on the starch chains had been demonstrated in our previous study.\textsuperscript{21}

Scanning electron microscopy (SEM) analysis has been known as an important means for clearly understanding granular structure of chemically modified starches and finding the most substituted regions on the starch granules.\textsuperscript{22} Accordingly, SEM analyses of HPSS and HS granules were carried out, and the SEM images of HPSS (b) and HS (a) are represented in Figure 3, for surveying the influence of hydroxypropylsulfonation on the granule morphology of cassava starch. There are no visible fissures on the surfaces of HS granules, whereas there has been visible damage on the surfaces of HPSS granules, indicating the alkaline condition and the reaction of starch hydroxyls with the CHPS-Na reagent on the granular surfaces might be the main reason of leading to the change in the surface topology of the granules.

**Influence of electrolyte species on phase separation rate of starch/PVA blend paste**

Influence of electrolyte species on ID\(_t\) of HPSS/PVA1799 blend paste and HS/PVA1799 blend one is depicted in Figure 4. In the figure, I, II, III, and IV denoted that no electrolyte, NaCl, Na\(_2\)SO\(_4\), and Na\(_2\)HPO\(_4\) were added into the paste, respectively. The concentration of the electrolytes was 0.05 mol/L while weight percentage of starch sample to the total sample was 50%. It could be seen that the addition of the electrolyte was able to reduce the ID\(_t\). This observation suggested that electrolytes increased the initial phase separation rate. As also seen from Figure 4, influence of three electrolytes on increasing the separation rate showed the tendency: Na\(_2\)HPO\(_4\) > Na\(_2\)SO\(_4\) > NaCl. In addition, irrespective of the addition of the electrolyte or not, the ID\(_t\) of HPSS/PVA1799 blend paste was more than that of HS/PVA1799 one. It meant that the modification could reduce the initial phase separation rate.

As is well known, starch is a carbohydrate polymer containing two inherently incompatible molecules: amylose and amylopectin.\textsuperscript{23} Normally, owing to the existence of hydrogen bonds formed between the hydroxyls in the starch molecules, starch granules in water show the characteristics...
of structural integrity and insolubility below its gelatinization temperature. Nevertheless, starch granules in water at high temperature will adsorb the water molecules and swell; meanwhile, their crystalline structure will be destroyed to form amorphous structure, eventually forming a cooked starch aqueous paste. The paste is generally known as an aqueous suspension of swollen fragments mainly consisting of the amylopectin that dispersed in a continuous phase described as the amylace aqueous solution. PVA aqueous solution is just a simple system of dissolving PVA macromolecules into water. Undoubtedly, the suspension characteristic of the starch paste will not produce some changes due to the incorporation of the PVA solution. In the successive phase of starch/PVA blend paste, phase separation behaviors are correlated with retrogradation of starch. As is well known, the macromolecules of linear amyloses have strong tendency of parallel arrangement due to the association of hydroxyls between the macromolecules in low-temperature aqueous paste, forming the aggregates. With the increase in the volume of the aggregates, the aggregates will present insolubility and subside from the paste, thereby leading to the phase separation behaviors. According to the principle of salting out, when electrolyte exists in starch paste, the electric field formed by ions dissociated from the electrolyte will result in the dissociation of water molecules that combine with starch hydroxyls. The water molecules will aggregate around the ions, accelerating the hydroxyl bonding between starch hydroxyls, thereby intensifying the aggregation speed of starch molecules, and subsidence rates of aggregates and swollen fragments of starch. This will cause the increase in the phase separation rate, that is, the decrease in the IDt, after the addition of the three electrolytes.

Undoubtedly, steric hindrance of the substituents can interfere with the re-association of starch hydroxyls and regular arrangement of starch amyloses in the paste, thereby helping to increase the combination of starch hydroxyls with water molecules and reduce the aggregation speed of starch macromolecules. As a result, the aggregates of water molecules around the ions will be weakened, thereby reducing the hydroxyl bonding and alleviating subsidence rates of the aggregates and swollen fragments of starch. Consequently, an increased IDt of the HPSS/PVA blend paste compared with that of HS/PVA one is obtained, as shown in Figure 4. The IDt indicated how fast a blend paste produced phase separation. Obviously, the higher the value, the better the stability of the blend paste. Therefore, a longer IDt of the blend paste implied that the hydroxypropylsulfonation was capable of improving the stability of starch/PVA paste.

**Influence of weight percentages of starch samples**

Undoubtedly, blending ratio of starch and PVA will produce a certain influence to phase separation rate. Therefore, its influence should be accessed. The results are illustrated in Figure 5. It could be found that IDt gradually decreased, and subsequently increased, as the weight percentage of starch sample raised. This observation suggested that weight percentage generated an obvious influence on the separation rate. In addition, at the same weight percentage,
IDt of HPSS/PV A1799 paste was longer than that of HS/ PV A1799 one. This also implied that HPSS/PV A1799 paste exhibited a lower separation rate and a better stability. Interestingly, HPSS/PV A1799 paste possessed higher stability when the weight percentage of HPSS sample was more than 70%. For the reason, increasing the content of HPSS sample in the size recipe will not only favor to reduce the cost, but also favor the improvement of the stability.

When the proportion of starch sample to PV A is low, the tendency of hydrogen bonding between PV A and hydroxyls of starch macromolecules enhances, which leads to the acceleration of initial phase separation rate. With the further increase in the proportion, initial phase separation rate decreases. With the further increase in the proportion, the content of PV A in the blend paste decreases, causing the reduction of the association of PV A hydroxyls and the increase in the hydrogen bonding between hydroxyls in the PV A and starch macromolecules. In addition, PV A macromolecules can produce a certain steric hindrance to hydrogen bonding between starch hydroxyls. Consequently, initial phase separation rate gradually decreases as the proportion further raises.

**Influence of concentration of NaCl**

Figure 6 describes the influence of concentration of NaCl on IDt of the blend paste. With the rise in the concentration, IDt gradually decreased. It confirmed that addition of the electrolyte not only produced an adverse influence on the separation rate but also generated a gradually enhanced adverse influence, that is, faster phase separation rate as its content raised.

In general, the higher the content of NaCl, the more the ions ionized, and the stronger the salting-out effect. As a result, water molecules associated with starch hydroxyls decrease, resulting in the increase in the association speed between starch hydroxyls, subsequently making the formation and subsidence rates of the aggregates of starch macromolecular increase. Consequently, the separation rate increases with the increase in the content.

**Influence of DS_h**

As is well known, end-use ability of a modified starch is correlated with its DS_h. Therefore, influence of DS_h on phase separation rate of paste is evaluated and depicted in Figure 7. When the concentration of NaCl was 0.02 mol/L, IDt of the blend paste depended on the DS_h. And with the rise in the DS_h, IDt increased at the same weight percentage of HPSS.

Apparently, with the increase in the amount of the HPS substituents introduced, their obstruction to the re-association of starch hydroxyls and the regular arrangement of starch amyloses in the paste gradually raise, making the combination of starch hydroxyls with water molecules
increase and the aggregation speed of starch macromolecules reduce. For the reason, the aggregates of water molecules around the ions will be gradually weakened, thereby a continuously reduced hydroxyl bonding, and the alleviated subsidence rates of aggregates and swollen fragments of starch are achieved. Consequently, an increased IDt is displayed as the DS_h raises.

**Influence of type of PVA**

In the 0.05 mol/L of Na_2SO_4, influences of degrees of polymerization and alcoholysis of PVA on the phase separation rates are investigated, as represented in Figure 8. It was clearly observed that, in the presence of Na_2SO_4, there was a slight difference between the IDt results of HPSS/PVA1799 paste and HPSS/PVA1788 one. This indicated that degree of alcoholysis showed little effect on the IDt at the same degree of polymerization, suggesting degree of alcoholysis had no significant impact on phase separation rate. In addition, it could be found that IDt results of HPSS/PVA0588 paste were much higher than those of HPSS/PVA1788 one at the same weight percentage of starch, implying low degree of polymerization favored the increases in the IDt results, thereby displaying a lower separation rate after blending the PVA with a low degree of polymerization. As a result, it could be noted that blending HPSS with PVA that had a lower degree of polymerization was capable of exhibiting a stronger paste stability.

**Conclusion**

The main objective of this work was to ascertain the influences of electrolytes and hydroxypropylsulfonation on paste stabilities of cassava starch/PVA blends. Based on the experimental results, it could be concluded that the addition of the electrolytes reduced the IDt, indicating the increase in the phase separation rate. With the rise in the concentration of NaCl, the IDt gradually decreased, thereby producing a gradually increased phase separation rate and reducing the paste stability of the blend paste. Hydroxypropylsulfonation was able to increase the IDt, thereby reducing the separation rate. The separation rate gradually reduced as the DS_h raised, thereby improving the stability of the blend paste. In addition, at the 0.05 mol/L of Na_2SO_4, blending HPSS with PVA that had a lower degree of polymerization was capable of exhibiting a stronger paste stability. The difference in the degree of alcoholysis had a slight influence on the separation rate.

**Declaration of conflicting interests**

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