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Short communication

Starch mono-phosphorylation for enhancing the stability of starch/PVA blend pastes for warp sizing

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Abstract

The effect of starch mono-phosphorylation on the stability of starch–polyvinyl alcohol (PVA) blend pastes is investigated for warp sizing. The stability is evaluated in terms of initial demixing time and subsidence ratio. The use of phosphorylated starch either as base material in the blended pastes or for enhancing the paste stability of native starch–PVA blends is investigated. The stability of phosphorylated starch–PVA blend pastes depends on the degree of modification of the starch. Phase separation does not occur within 24 h if the DS value ≥ 0.049. The starch monoester can also be used as stabilizer to increase paste stability. Increasing the degree of phosphorylation and/or amount of the starch monoester effectively retards the separation rates and enhances paste stability.

Keywords: Warp sizes; Starch phosphate; Polyvinyl alcohol; Paste stability

1. Introduction

Starch and polyvinyl alcohol (PVA) are very useful in textile industry as sizing agents. They are commonly used in a form of blended pastes for sizing synthetic/cellulose blend spun yarns (Zhu, Zhou, & Zhang, 1995). However, the blended pastes separate with time on standing (Zhu, 2000), because starch is not thermodynamically compatible with PVA. In sizing operations, the separation phenomenon occurs both in sizing boxes and on surface of sized yarns before drying. The sizing pastes will precipitate if the separation is too extensive. Precipitation alters the ingredient content of sizing pastes and induces sizing defects such as starch marks, uneven size add-on, and more warp hairiness (Chen, 1991). Therefore, unstable sizing pastes are very harmful to the qualities of sized yarns. For this reason, paste stability has received much recent attention.

However, like many industrial applications, for warp sizing it is not essential that the components of the size are miscible. Sizes with immiscible components can be used if they can be processed to a relatively stable and even paste. The behavior corresponding to the stability of a blended mixture is often named as mechanical compatibility (Traugott, Barlow, & Paul, 1983). It does not mean that the free energy of mixing $\Delta G_m \leq 0$, but only requires that the blended mixture is stable and well-distributed. Therefore, studies on paste stability for warp sizing should not be considered from a thermodynamic viewpoint. Since, the only result obtained may be that starch and PVA are immiscible. This is widely known and is no help in improving the warp sizing operation. In this study, an attempt has been made to enhance the stability of starch–PVA blend pastes through starch phosphorylation. Consequently, we directed our efforts toward studying the separation behavior of starch–PVA blends, investigating the influence of starch phosphorylation upon paste stability, and also explored the possibility of using the modified starch as a stabilizer to enhance the paste stability of native starch–PVA blends.

2. Materials and methods

Commercial cornstarch with a paste viscosity of 150 mPa s (6%, 95 °C, 1 h after starch gelatinization, and determined by NDJ-79 viscometer) was supplied by the Hongguang Starch Co. Ltd, Hebei Province. Prior to use, the starch was purified in accordance with our previous studies (Zhu & Zhuo, 2001a,b). PVA 1799 (hydrolysis degree

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≥99%; $\overline{DP} = 1700$) was made in the Chongqing Reagent Factory (Sichuan Province) and lost 7.74% on oven drying. PVA 1788 (hydrolysis degree = 88%; $\overline{DP} = 1700$) with a volatile content of 4.46% was supplied by the Sichuan Vinylon Factory (Sichuan Province). Sodium dihydrogen phosphate and sodium hydrogen phosphate were all chemically pure grades.

Equal moles of sodium dihydrogen phosphate and sodium hydrogen phosphate were dissolved in 90 ml of distilled water and the phosphate solution was heated to 50 °C. 0.37 mol (60g) of refined native cornstarch was added into the solution and stirred for 30 min. The starch dispersion was filtered and the starch cake was oven-dried at 65 °C to a moisture content of less than 10%. The starch containing the impregnated orthophosphates was placed in an oven and reacted at 145 °C for 2 h. The product was ground and washed with 100 ml of ethanol–distilled water (50:50 by volume) three times to eliminate the residual phosphate. Finally, the product was dried, ground and sieved to pass through a 100 mesh-sieve.

The apparent viscosity was measured by using a rotary viscometer (NDJ-79) with a shear rate of 344 s^{-1} at 95 °C (Fan & Ding, 1997).The phosphorus content of the starch phosphate prepared was determined by a spectrophotometric method (Fan & Ding, 1997) at 825 nm. The degree of substitution of the modified starch was calculated from the phosphorus content (P%).

The preparation of the blended pastes, and the measurement of the paste stability were conducted in accordance with our previous studies (Zhu, 2000; Zhu & Li, 2002).

3. Results and discussion

The initial demixing time denotes how fast a blended paste will separate. Obviously, the bigger the value the better is the stability of the blended pastes. The subsidence ratio represents the separation extent of the blended pastes. Under the same blend proportion of starch to PVA, the smaller the subsidence ratio, the less the PVA phase separated and the better the stability of the pastes. The phosphorus content, degree of substitution, and apparent viscosity of the starch samples are given in Table 1.

Table 1
The apparent viscosity and DS values of starch phosphate monoester

Sample number	Phosphorus content (%)	Degree of substitution	Apparent viscosity (mPa s)[a]
Native starch	/	/	150
1#	0.238	0.013	270
2#	0.515	0.028	260
3#	0.895	0.049	80

[a] The concentration of the pastes for viscosity measurement was 6%.

3.1. Effect of starch mono-phosphorylation

The effect of starch phosphorylation on paste separation is presented in Figs. 1 and 2. It is clearly seen that, no matter what type of PVA is involved in the blended pastes, phosphorylation extends the initial demixing time and the subsidence ratio decreases. This suggests that the initial rates of the paste separation are reduced and the separation extent of the blended pastes is decreased. Consequently, the phosphate modification enhances the paste stability. Moreover, the degree of substitution of the starch phosphate monoester also plays an important role in enhancing the paste stability. Fig. 1 shows that the separation rates are reduced with increasing DS values. Phase separation did not occur within 24 h when the DS of the modified starch equals 0.049. Fig. 2 only gives the subsidence ratios of the blended pastes containing the modified starch with DS = 0.013, because the separated interfaces of the blended pastes were too indistinct to recognize when the DS value was 0.028. These results demonstrate that increasing the extent of phosphorylation enhances paste stability.

It has been shown that pure starch pastes can be described as suspensions of swollen particles dispersed in a macromolecular medium (Doublier, Llamas, & Le Meur, 1987; Wong & Lelievre, 1982). The swollen starch particles are mainly composed of entangled amylopectin, whereas the continuous phase is a solution of the soluble fraction. The principal ingredient of the soluble fraction in cornstarch pastes is amylose solubilized from the starch granules in the gelatinization process. On the other hand, aqueous PVA solution is only a simple homogenous system of PVA macromolecules dissolved in water. When starch pastes are mixed with PVA solutions, the swollen starch particles must initially be dispersed in a continuous medium comprising the soluble starch fraction and the dissolved PVA. Starch subsidence in dilute starch–PVA pastes has be observed as a process involving two steps (Zhu, 2000). One is the association of the hydroxyls within the amylose and converting the dissolved amylose into numerous aggregates. Another is the subsidence of these aggregates in conjunction with the swollen starch granules. These two steps are often involved in phase separation and starch subsidence. Therefore, significant retrogradation of gelatinized starch occurs and the blended pastes lose their original clarity. This has been shown in our previous investigation (Zhu, 2000). Starch mono-phosphorylation enhances the hydrophilicity of both amylose and amylopectin. In addition, the presence of the substitute groups interferes with amylose aggregation in the continuous phase. These two factors inhibit aggregate formation and the subsidence of these aggregates in conjunction with swollen starch granules. Furthermore, phase separation is unfavorable between a polyelectrolyte and a non-polyelectrolyte because of the entropic effect resulting from uneven distributions of ions in the different domains. Therefore, the mono-phosphate modification of

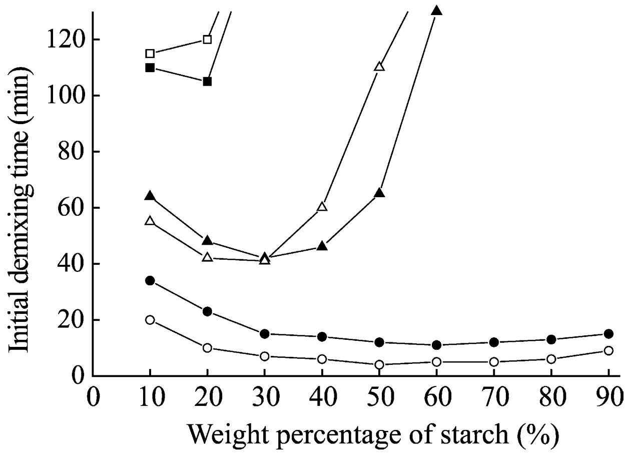


Fig. 1. Effect of starch phosphorylation on the initial demixing time of the blended pastes. Paste compositions: starch/PVA 1799 (solid symbols); starch/PVA 1788 (open symbols). Starch type: for native starch, circles; for starch phosphate: DS = 0.013 (triangles); DS = 0.028 (squares).

starch would greatly reduces the separation of the blended pastes.

3.2. Effect of starch phosphate as a stabilizer

The effects of using starch phosphate monoester as stabilizer are shown in Fig. 3. When compared with Fig. 1, these are evident differences in initial demixing time depending upon the use of the stabilizer and upon the extent of starch modification both for partially and fully hydrolyzed PVA. The addition of the starch phosphate increases substantially the values of the initial demixing time especially when the proportion of starch to PVA is high, which shows that the initial rates of phase separation are reduced. Moreover, the separation rates are also clearly reduced on increasing the degree of substitution although the subsidence ratios of the blended pastes containing the lowest proportions of starch shows no DS sensitivity. Such a tendency can be ascribed to the amounts of the stabilizer involved in the blended pastes.

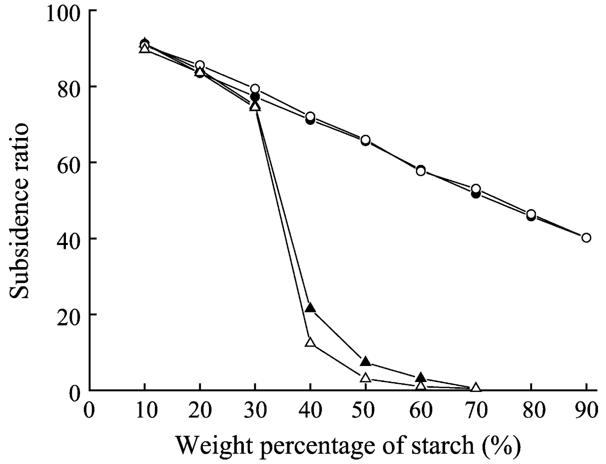
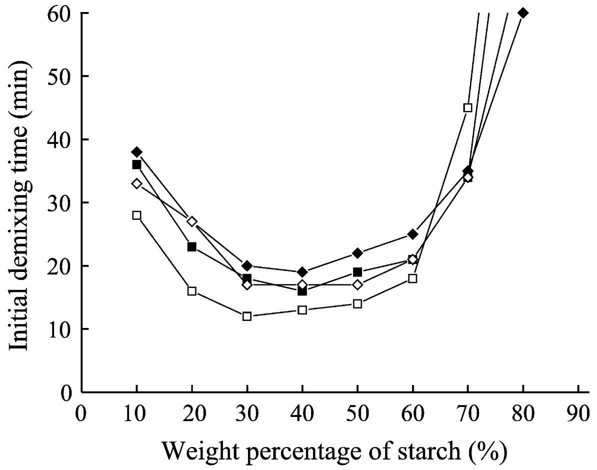
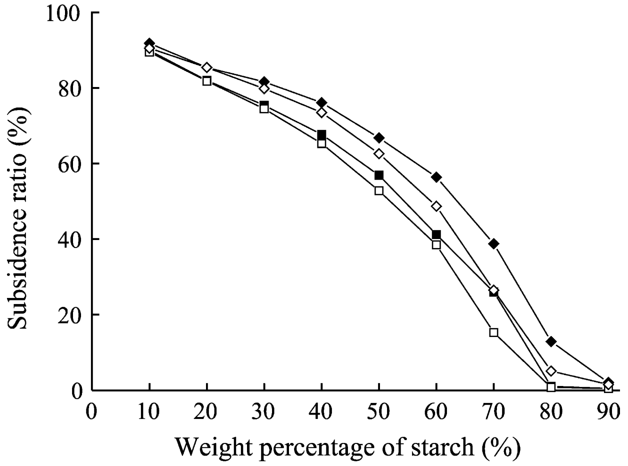


Fig. 2. Effect of starch phosphorylation on the subsidence ratio of the blended pastes (The symbols here express the same meaning as in Fig. 1). (a) Initial demixing time (min). (b) Subsidence ratio (%).



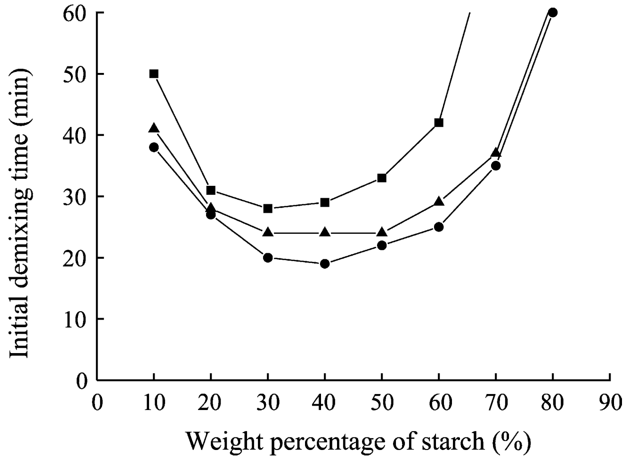
(a) Initial demixing time (min)



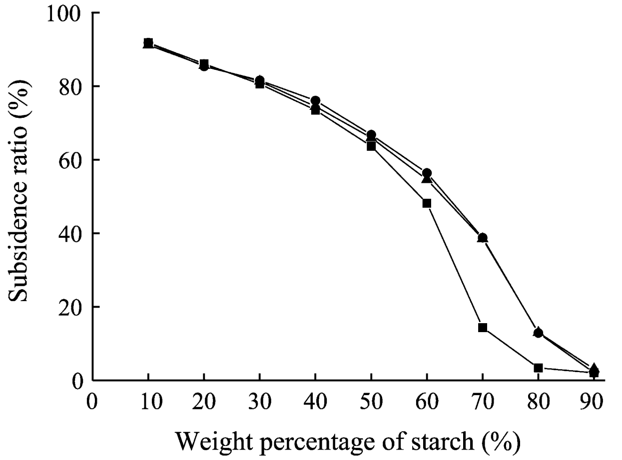
(b) Subsidence ratio (%)

Fig. 3. Effect of starch phosphate monoester as stabilizer on the separation of the blended pastes (The weight proportion of the modified starch to native starch is 15:85). Paste compositions: starch phosphate monoester/-native starch/PVA 1799 (solid symbols); starch phosphate monoester/native starch/PVA 1788 (open symbols). DS of starch phosphate monoester: for 0.028 (squares); for 0.049 (rhombuses).

In native starch–starch phosphate–PVA blend pastes, special attention should be paid to starch mono-phosphate that influences the aggregation and subsidence of native starch. Our experiments demonstrated that native starch separated in these three component blends. It can be speculated that much of the phosphorylated starch molecules tend to exist within the native ones because their molecular structures are similar. As one might be intuitively expected, the coexistence of native starch with the modified starch interferes with the aggregation and subsidence of the former. The formation of starch aggregates containing native starch and a small amount of phosphorylated starch would be reduced. Furthermore, even if the aggregates are formed, the phosphorylated starch within the aggregates



(a) Initial demixing time (min)



(b) Subsidence ratio (%)

Fig. 4. Effect of the starch phosphate amounts on the separation of starch phosphate–native starch–PVA 1799 blend pastes (DS of starch phosphate was 0.049). Starch compositions: for starch phosphate monoester/native starch = 15/85 (●); 25/75 (▲); 40/60 (■).

tends to enhance their hydrophilicity and retard their subsidence. Therefore, the separation rates are reduced and the paste stability is increased. Besides, the bigger the DS the greater the interference with aggregation and subsidence, and the more stable the blended pastes are within the range covered by our experiment.

3.3. Effect of stabilizer amount

The dependence of the paste stability on the stabilizer amount has been investigated over the range 15–40%. Fig. 4 indicates that the separation rate depends upon the amount of the modified starch. With increasing the amounts, the separation rates are reduced and the paste stability is raised. This may be mainly attributed to the increased interactions between the phosphorylated starch and the native one, and to the enhanced interference with aggregate formation and subsidence. On the other hand, the increase in the amount of starch phosphate monoester only results in a very limited decrease in subsidence ratios. This implies that the separation extent could not be significantly reduced by increasing the stabilizer amount. It should be noted that even if the amount of starch phosphate is as high as 40%, the phase separation is still occur, but the separation rates are clearly reduced.

Acknowledgements

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