

Monophosphorylation of Cornstarch to Improve Its Sizing Properties for Heat-Sensitive Wool Yarns at Reduced Temperature

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ABSTRACT: Commercial cornstarch was mono-phosphorylated to different levels of substitution in order to investigate the effect of phosphorylation on the properties of cornstarch for sizing heat-sensitive wool yarns at reduced temperature. The influences of starch phosphorylation and sizing temperature upon apparent viscosity and viscosity stability of cooked starch paste, starch retrogradation, adhesion to wool fibers, performance of starch film, aerobic biodegradation, mechanical properties, and hairiness of sized wool yarns were evaluated. The phosphorylation level was varied from 0.021 to 0.082 in degree of substitution (DS), while the temperature considered was from 60 to 95°C. It was found that mono-phosphorylation of starch resulted in enhanced paste stability, reduced retrogradation, strong adhesion to wool fibers, increased performances of starch film, improved mechanical properties of sized wool yarns, and decreased hairiness on surface of sized yarns even if paste temperature was lowered to 60°C. Initially increasing phosphorylation level enhanced positive effects, but excessively increasing the level was not applicable due to marked reduction in tensile strength of starch film. The phosphorylation with a DS value of 0.061 could improve the performances of cornstarch for sizing wool yarns at 60–80°C. Moreover, measurement on BOD₅/COD ratios demonstrated that the phosphorylation did not impede aerobic biodegradation of starch. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: modified starch; warp sizing agent; phosphorylation; wool yarn; sizing temperature

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INTRODUCTION

Industrial concern on sizing operation of the warps which are spun from heat-sensitive fibers like wool has now resulted in research interests in improving sizing performance of starch used as sizing agents for sizing wool yarns at reduced temperature. As is well known, wool fibers are sensitive to hot water. Tensile strength and breaking elongation of wool yarns are reduced after they have been subjected under high temperature and wet processes like sizing operation.¹ The reduction is seriously harmful to weaving operation because the yarns are not able to withstand repeated drawing and bending. Yarn damage and break occur, thereby reducing weaving efficiency, decreasing quality of fabrics produced, and increasing labor intensity during textile production.¹ For this reason, wool warps are generally required to be treated under lower temperature.

Wool warps are currently sized with spin finishes and synthetic sizes. However, oiling on surfaces of wool yarns with spin finishes can not meet weaving requirements of fine and single-

strand wool warps. Therefore, synthetics have to be used nowadays. The synthetics currently used are usually compounds such as lower molecular-weight polyvinyl alcohol (PVA) and polyethylene glycol (PEG).² They are not only expensive but also less biodegradable than natural ones, thereby inducing economic and environmental problems. It is generally accepted that PVA in desizing waste biodegrade slowly in nature.² Previous investigation has confirmed that the rate and extent of PEG biodegradation decrease with increasing its chain length because higher molecular-weight PEGs are too large to be penetrated by bacteria.³

Starches are biodegradable, cheap and abundant⁴ because they are natural renewable polysaccharide obtained from a great variety of crops. Starches can be used as one of the raw materials for sizing cotton, hemp, flax, ramie, and synthetic yarns in cotton mill at 95–99°C.² However, cooked pastes of some native starches such as corn and wheat ones tend to form rigid and opaque gels⁵ while cooling, i.e., aging or retrogradation.

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Retrogradation is a term given to the changes that occur in a starch paste or gel while aging⁶ and has been defined as a process during which gelatinized starch returns from a solvated, dispersed or amorphous state to an insoluble, aggregated, or crystalline state.⁷ This characteristic leads to weak adhesion to fibers and excessive fluctuation of paste viscosity under lower temperature.² Generally, native starches are not applicable in sizing wool yarns due to these shortcomings in physicochemical properties such as low paste stability, high retrogradation tendency, weak adhesion, and brittle film. Therefore, an effort had been made to improve its sizing performance through chemical modification for heat-sensitive wool yarns.

Starch phosphate monoester is one of the commonly used starch derivatives which can be adopted to meet the needs of many ultimate uses in miscellaneous applications.^{8,9} Phosphate groups can be introduced onto starch backbones through “dry heat” reactions of starch with ortho-, pyro-, or triphosphates.^{9–12} The phosphate groups introduced weaken starch recrystallization due to steric restriction and hydrophilic behavior of the groups. Therefore, phosphorylation may be capable of depressing the shortcomings like retrogradation and improving sizing ability of starch for sizing wool yarns. In previous study, Sitohy and Ramadan¹³ examined the degradability of phosphorylated starch film and reported that the film showed better degradability by α -amylase than the ones prepared from non-phosphorylated starch. Recent investigation¹⁴ indicated that the phosphorylation-impeded retrogradation of rice starch paste. Moreover, the phosphorylation enhances endurance of starch to electrolyte impurities in aqueous paste.¹⁵ These progresses lay a foundation for improving the properties required in wool yarn sizing.

The aim of this study was to reveal the effect of starch phosphorylation on the properties of sized wool yarns at reduced temperature. Accordingly, we made our efforts toward studying mechanical properties of the yarns sized with phosphorylated starch at reduced temperature. Moreover, the influence of phosphorylation level upon apparent viscosity, viscosity stability, adhesion to wool fibers, and starch film were also evaluated because these performances often depended on the level of starch modification. Furthermore, aerobic degradation of phosphorylated starch was assessed by measuring the BOD₅/COD ratio and comparing the ratios of phosphorylated starch with those of native starch, PVA, PEG, and bone glue for evaluating environmental behavior of phosphorylated starch.

EXPERIMENTAL

Materials and Chemicals

Commercial native cornstarch with an apparent viscosity of 60 mPa s and a viscosity instability of 21% was supplied by Xingmao Corn Develop (Zhucheng, Shandong, China). Chemicals such as sodium dihydrogen phosphate, sodium hydrogen phosphate, urea, hydrochloric acid, and sodium hydroxide were available commercially from Sinopharm Chemical Reagent, Tianjin Damao Chemical Reagent, Shenyang Third Reagent Factory, Nanjing Shengyue Fine Chemical Reagent, and Wuxi Yasheng Chemical Reagent, China, respectively. They were all analytical reagent grades and were used directly.

Pure wool roving (386 tex, twist factor: 5) obtained from Yuanda Textile (Zhangjiagang, Jiangsu Province) was used in adhesion measurement. Fiber length and quality number of wools in the roving were 80.4 mm and 64, respectively. Totally, 100% wool yarns used in sizing procedure were ring-spun ones, 25 tex, and were also obtained from Yuanda Textile. Tensile strength and breaking elongation of the yarns were 162.3 cN/tex and 18.83%, respectively, and their corresponding coefficients of variation for tensile strength and elongation were 13.84% and 25.43%. Hairiness indexes of unsized wool yarns in length intervals of ≥ 3 mm to 4 mm, ≥ 4 mm to 5 mm, ≥ 5 mm to 7 mm, ≥ 7 mm to 10 mm, and ≥ 10 mm were 32.5, 21.08, 11.58, 5.95, and 1.7, respectively.

Starch Modification

To use starch satisfactorily in warp sizing, apparent viscosity of gelatinized starch paste must be reduced so as to raise the impregnation of sizing paste into warp yarns.¹⁶ For this reason, native corn starch was hydrolyzed with HCl before phosphorylation. The acidification was carried out in an aqueous suspension by dispersing 300 g starch (dry basis) into 500 mL of distilled water. The suspension was transferred into a flask and heated under mechanical stirring. When the temperature of the suspension was raised to 50°C, 27 mL of dilute HCl solution (2 M/L) was added. The acidification was carried out under continuous stirring at 50°C for 180–270 min (180 min for nonphosphorylated starch, and 210, 230, 250, and 270 min for the phosphorylated starch samples with the DS values of 0.021, 0.048, 0.061, and 0.082, respectively). Then, the product was neutralized with 1% NaOH solution, filtered, washed carefully with distilled water, dried at 60°C, pulverized and sieved to pass through a 100 mesh-sieve.

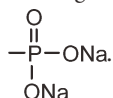
Then, 4 g of urea, 2.5 g of Na₂HPO₄, and 2.5 g of NaH₂PO₄ were dissolved into 285 mL of distilled water. Two hundred grams of acid-thinned starch (dry weight) was dispersed in the phosphate solution. After the dispersion had been stirred mechanically for 30 min, the starch was filtered by suction to form cake with about 45% moisture content. The cake was dried at 60°C to a moisture content of $\sim 14\%$, pulverized and sieved through passing a 100-mesh sieve. And then, the starch was further dried to moisture content below 8%, heated to 150°C, and phosphorylated at the temperature for 2 h. Finally, the product was washed to remove residual phosphate as our previous study,¹⁵ dried at 60°C for about 8 h, ground and sieved through passing a 100-meshed sieve. The degree of substitution of phosphorylated starch prepared was 0.021. The phosphorylated starches with the degrees of substitution of 0.048, 0.061, and 0.082 were prepared by increasing the weights of both Na₂HPO₄ and NaH₂PO₄ to 5, 10, and 15 g, respectively.

Starch Characterization

Phosphorus content of purified starch was measured spectrophotometrically at 825 nm.⁸ Degree of substitution (DS) was calculated on the basis of bonded phosphorus from phosphorus content as follow¹⁵:

$$DS = \frac{162(P - P_0)}{3100 - 124(P - P_0)} \quad (1)$$

where P (%) and P_0 (%) were phosphorus contents of purified phosphorylated starch and native starch, respectively. In this formula, the constant of 162 denoted molar mass of glucose units of starch; 3100 was the product of phosphorus mole mass multiplied by 100; 124 corresponded to the difference of subtracting mole mass of hydrogen from that of phosphate group



Apparent viscosity and viscosity stability of cooked starch pastes were measured using an NDJ-79 rotary viscometer (Tongji Electrical Machinery Plant, Shanghai, China) by the method¹⁷ reported previously only with an exception in temperature. The temperatures of starch pastes during the measurement were 95, 80, and 60°C, respectively.

Light Transmittance of Starch Paste

Light transmittance of cooked starch pastes was tested by Craig's method.¹⁸ Starch was pasted by dispersing 4.0 g (dry basis) of starch in 396 mL of distilled water, heated to 95°C, and maintained at the temperature under mechanical stirring for 1 h. After the paste had been cooled to 80 or 60°C, respectively, and kept at the temperatures for 3 h, light transmittance was measured with a HY722 spectrophotometer at 660 nm against distilled-water blank. The values reported were mean value of two separate tests for each case.

Measurement on COD₅ and BOD

Chemical oxygen demand (COD) was measured by a standard method for the examination of water and wastewater.¹⁹ 10 mL of potassium dichromate (0.250 mol/L) was added into 20 mL of starch sample (0.1 g/L). Sulfuric acid, silver sulfate, and ferrous were added in sequence. After refluxing, nonreduced potassium dichromate was titrated with ammonium ferrous sulfate (0.10 mol/L). The amount of ammonium ferrous sulfate reacted was converted to COD through eq. (2):

$$\text{COD (mg O}_2\text{/L)} = \frac{C(V_1 - V_2) \times 8000}{V_0} \quad (2)$$

where C (mol/L) was the concentration of ammonium ferrous sulfate standard solution; V_1 (mL) and V_2 (mL) were the volumes of ammonium ferrous sulfate standard solution in blank and sample test, respectively; V_0 (mL) was the volume of sample solution; "8000" was the conversion value of molar mass of O₂ (mg O₂/L).

Biological oxygen demand within 5 days (BOD₅) was determined by standard BOD₅ tests¹⁹ using sludge from a local lake. The determination measured the relative oxygen requirements of starch sample. The method consisted of filling with sample into an airtight bottle and incubating the sample at 20 ± 1°C for 5 days. Dissolved oxygen was measured before and after incubation, the BOD₅ was calculated from the difference between initial and final dissolved oxygen.

The COD and BOD₅ data reported were the mean values of three individual tests for each case.

Adhesion to Fibers

Recently, the measurement on the adhesion of starch to fibers became a legal method (FZ/T 15001-2008) regulated by China

Cotton Textile Association. Currently, textile technicians have been used to this legal method and are quite familiar with the values measured for the determination of technical parameters during warp sizing operation. For this reason, FZ/T 15001-2008 was adopted for the evaluation of the adhesion. On the basis of the regulation, wool roving was used as adherent to measure the adhesion of starch to wool fibers by subjecting the roving to drawing test to failure. Tensile loads were adopted to exhibit the adhesion.^{17,20-22} The measurement was as follows:

Starch was pasted by dispersing 22.0 g (dry basis) of starch in 2178 mL of distilled water, heated to 95°C and kept at the temperature under mechanical stirring for 1 h. The paste was shifted to three metal vessels immersed in water bath of 95, 80, and 60°C, respectively. After the paste in the vessel had been kept at the temperatures for 3 h, the rovings carefully wound onto three frames were impregnated respectively with the pastes in three vessels for 5 min. Then the impregnated rovings were dried in air. After had been kept at 65% relative humidity and 20°C for 24 h, the rovings were measured on an YG065H Tensile Tester (Laizhou Instrument, Shandong China) for tensile strength (S_t), breaking extension (E_b), and work-to-break (W_b) under the condition described in Ref. 17.

Performances of Starch Film

Starch film was cast and measured in accordance with the method described in our previous publication.¹⁷ Four hundred grams of cooked starch paste (6%, w/w) was completely poured onto a 650 mm × 400 mm polyester film spread on a same size glass plate and dried under ambient condition of 65% relative humidity and 20°C. Then, the film obtained was tailored into strips with a size of 200 and 10 mm in length and width. After the stripped films had been kept under above condition for 24 h, tensile strength, breaking elongation, and work-to-break of the films were measured on a BZ2.5/TNIS Zwick Material Tester (Zwick, Ulm, Germany) with an initial chuck-distance of 100 mm and a drawing speed of 50 mm/min under same ambient condition. Twenty samples were measured to obtain the mean value for each data reported.

Sizing Procedure

A JSSJ-83 Miniature Sizing Machine (Taixian Textile Machinery Plant, Jiangsu, China) was adopted to size wool yarns at a speed of 5 m/min with a warp density of 316 ends per 10 cm. Starch paste was cooked with mechanical agitation at a concentration of 10%. After starch had been gelatinized for 1 h, the paste was shifted into the sizing box on the machine. The yarns were impregnated with the paste at 95, 80, or 60°C respectively, and squeezed with a pair of weighed roller at squeezing pressures of 6.9 N/cm and 10.8 N/cm, respectively, for front and back rollers. Finally, the sized yarns were dried with four drying cans and wound onto a small beam.

Measurement on Sized Yarns

Tensile strength and breaking elongation of sized wool yarns were tested on a HD021N Tensile Tester (Nantong Hongda Instrument, Jiangsu, China) under 65% relative humidity and 20°C in accordance with American Society for Testing and Materials D 2256 under a test length of 500 mm and an initial tension of 7.3N. Yarn-drawing was performed by controlling tension increment at a rate to reach their breaking force in an

Table I. Paste Characteristics of the Phosphorylated Starch at Different Temperatures

Degree of substitution	95°C		80°C		60°C	
	Viscosity (mPa s)	Viscosity stability (%)	Viscosity (mPa s)	Viscosity stability (%)	Viscosity (mPa s)	Viscosity stability (%)
0	17.5	89	18.5	78	23.0	60
0.021	15.5	90	19.0	90	22.0	72
0.048	14.0	92	17.5	90	25.0	78
0.061	15.5	86	18.0	85	28.0	81
0.082	16.5	85	18.0	85	36.0	82

average time of 20 ± 3 s from the start of the test. For each yarn sample, 50 pairs of tensile strength and breaking elongation readings were measured and their mean values were used to calculate the increase in tensile strength (I_{ts} %) and loss in elongation (L_e %) from eqs. (3) and (4).

$$\text{Increase in tensile strength (\%)} = \frac{S - S_0}{S_0} \times 100\% \quad (3)$$

$$\text{Loss in elongation (\%)} = \frac{E_0 - E}{E_0} \times 100\% \quad (4)$$

where S and S_0 were the mean values of tensile strength of sized and unsized yarns. E and E_0 were the mean values of breaking elongation of sized and unsized yarns, respectively.

Abrasion resistance of wool yarns under tension was evaluated in average number of abrasion cycles (N_{ac}) to break. The number was measured using an Y731 Abrasion Tester (Changzhou Textile Instrument Plant, Jiangsu, China) under above atmosphere condition with a preliminary tension of 19.6 cN per end and an abrasion speed of 120 rpm. The values reported were the average number of abrasion cycles to break for 30 tests.

Hairiness on the yarns was evaluated in term of decrease in hairiness (D_h %). The hairiness was determined using an YG173 Hairiness Tester (Suzhou Changfeng, Jiangsu, China) in accordance with International Standard ASTM D 5647-01 with an exception of test length. The tester counts the number of hairs which are longer than 3 mm in a 300 m length, instead of 100 m. The hairs were classified according to their length into five length intervals, i.e., >3–4 mm, >4–5 mm, >5–7 mm, >7–10 mm, and >10 mm. Decrease in hairiness (%) was calculated using eq. (5):

$$\text{Decrease in hairiness (\%)} = \frac{H_0 - H}{H_0} \times 100\% \quad (5)$$

where H and H_0 were the mean values of hairiness on sized and unsized yarns, respectively.

Size add-on (%) refers to a weight percentage of the sizes on warps to the yarns to be sized. It was determined with an acid-desizing method. The principle of this method was to remove the sizes from sized yarns by boiling the yarns in dilute sulfuric acid, and then the weight loss of the samples was used for the

calculation of size add-on. Experimental procedure was in accordance with our previous publication.²³

RESULTS AND DISCUSSION

Effect on Starch Paste

Table I shows the influences of paste temperature on apparent viscosity and viscosity stability of cooked starch paste under different levels of starch mono-phosphorylation. It can be observed that the viscosity increases as paste temperature decreases. Obviously, the increase in viscosity is mainly attributed to the increased intermolecular forces between starch and water when the temperature decreases. Apparent viscosities of the modified starch samples with different phosphorylation levels do not show much change at 80 and 95°C. This is mainly attributed to the acidification before starch phosphorylation since the acidification balances the increase in viscosity caused by the phosphorylation. The increase in viscosity at 60°C is due to, in addition to the increased intermolecular forces between starch and water, the association of hydroxyls between starch molecules. Currently, the viscosity of starch sizing agents used for warp sizing is about 10–40 mPa s, which is quite in accordance with the viscosity of the starches prepared. On the other hand, phosphorylation shows positive effect on viscosity stability of cooked starch paste at 60 and 80°C compared with the nonphosphorylated starch. The stability of phosphorylated starch paste increases substantially at 60°C as phosphorylation level rises. This is a valuable behavior for a modified starch used in warp sizing because stable size add-on required during sizing operation is intensely related to the stability. The ineffectiveness of mono-phosphorylation in improving viscosity stability of cooked starch paste at higher temperature may be probably due to partial hydrolysis of glucosidic bonds in starch backbones because the bonds are sensitive to high temperature.² However, the phosphate groups introduced onto starch backbones can prevent the formation of hydrogen bonds of starch hydroxyls under low temperature due to their steric effect, which favors the increase in viscosity stability of starch paste at reduced temperature.

Light transmittance of cooked starch paste at different temperatures is presented in Figure 1. It is clearly seen that non-phosphorylated starch paste shows a steady drop in the transmittance as paste temperature decreases, whereas the phosphorylated ones are resistant to the temperature variation. The observation means that the phosphorylation is capable of

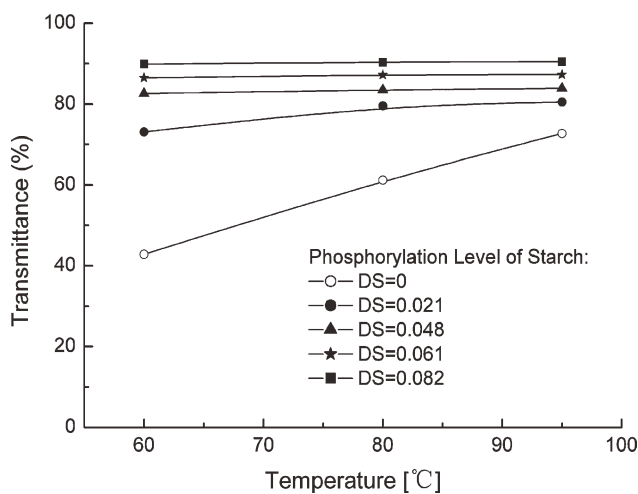


Figure 1. Light transmittance of starch paste at different temperatures.

depressing the retrogradation of starch paste under reduced temperature. Moreover, increasing phosphorylation level initially favors the depression. However, little benefit is observed regarding the depression at higher levels of phosphorylation.

As is well known, starch contains two different structures: linear amylose and branched amylopectin.²⁴ When native starch paste cools down, it converts gradually into an opaque, nonfluent and semisolid substance called gel through retrogradation. This phenomenon is mainly attributed to the association of the hydroxyls between amylose chains.² The association results in regular arrangement of amylose and converts dissolved amylose into macromolecular aggregates.⁸ It is the aggregates that stop light transmittance. Under lower temperature, there is an increased hydrogen interaction within starch paste, thereby restraining the movement of starch molecules.²⁵ Therefore, the transmittance decreases with the decrease of paste temperature (above 0°C). Mono-phosphorylation of starch introduces hydrophilic phosphate groups and increases dispersability of starch in aqueous pastes. The phosphate groups introduced disturb the association of starch hydroxyls and interfere with regular arrangement of amylose due to their steric hindrance. Therefore, a clear and stable paste under lower temperature is observed. It has been elucidated that the retrogradation occurs when the molecules of gelatinized starch begin to re-associate in an ordered structure.⁶ Because of the steric hindrance of phosphate groups, the retro-

gradation is restrained. Increasing the modification level up to a DS of 0.048 or above is favorable to prevent the retrogradation of starch paste.

Effect on Adhesion to Wool Fibers

Influences of starch phosphorylation and paste temperature on the adhesion of starch paste to wool fibers are shown in Table II. Generally, tensile strength indicates the bonding strength of sizing agents to fiber substrates. The greater the strength, the stronger is the adhesion.²¹ Breaking extension could be used to evaluate the toughness of the bonding at room temperature. The larger the extension, the tougher the bond is.²¹ Work to break expresses an ability of the bonding to resist impact break by bonding. Consequently, they are all the measurements on the adhesion of sizing agent to fibers. Table II indicates that the variation in adhesion depends not only on the phosphorylation level, but also on the temperature. For the nonphosphorylated starch, tensile strength, breaking extension, and work-to-break decrease with the decrease in paste temperature. This means that the adhesion decreases as paste temperature decreases. However, the strength, extension, and work do not show much sensitivity to the variation of paste temperature when DS value of starch phosphate reaches or exceeds 0.061. Apparently, the modification enhances the adhesion of starch to wool fibers particularly under lower temperature. Increasing the modification level up to 0.061 is necessary to enhance the adhesion.

Obviously, starch retrogradation in aqueous paste induces non-homogeneous paste and results in incomplete wetting and spreading of starch paste onto surface of fibers. In this case, interfacial defects and stress concentration around unwetted or outspread areas occur. It has been elucidated that the incomplete wetting and spreading is deleterious to the adhesion.²⁶ For this reason, the adhesion of the nonphosphorylated starch to the fibers decreases as paste temperature decreases. Mono-phosphorylation of starch introduces hydrophilic phosphate groups, thereby increasing starch dispersability in aqueous pastes under lower temperature. And steric hindrance of phosphate groups introduced exhibits a certain extent of resistance to starch retrogradation due to the disturbance to the association of starch hydroxyls and the interference with the regular arrangement of amylose. Therefore, the modification improves the wetting and spreading of starch paste onto fibers. In addition, phosphate groups are hydrophilic and are capable of absorbing water into adhesive layers between fibers.¹⁵ The layers are formed by starch

Table II. Effect of Starch Mono-phosphorylation on the Adhesion of Starch to Wool Fibers at Different Temperatures

DS values	95°C			80°C			60°C		
	S_t (cN/tex)	E_b (%)	W_b (J)	S_t (cN/tex)	E_b (%)	W_b (J)	S_t (cN/tex)	E_b (%)	W_b (J)
0	10.1 (12.6)	5.64 (9.25)	0.110 (15.2)	9.5 (10.9)	5.28 (9.75)	0.097 (12.8)	7.9 (13.4)	4.83 (12.4)	0.073 (12.5)
0.021	11.5 (11.8)	6.21 (8.83)	0.138 (11.5)	11.1 (10.6)	6.17 (7.62)	0.132 (10.8)	10.5 (11.3)	5.78 (10.8)	0.117 (15.1)
0.048	13.1 (11.4)	6.59 (8.39)	0.167 (13.2)	12.9 (10.8)	6.42 (9.43)	0.160 (11.2)	12.9 (10.9)	6.54 (11.1)	0.162 (13.4)
0.061	14.4 (9.69)	7.02 (9.24)	0.196 (10.7)	14.5 (11.3)	6.93 (8.68)	0.194 (9.87)	14.7 (10.3)	7.08 (10.3)	0.200 (11.5)
0.082	14.6 (12.3)	6.98 (7.17)	0.197 (14.6)	14.8 (10.7)	7.11 (10.6)	0.202 (13.1)	14.7 (10.3)	6.94 (9.87)	0.198 (9.48)

The data in blanks are the coefficients of variation (%) of the corresponding data.

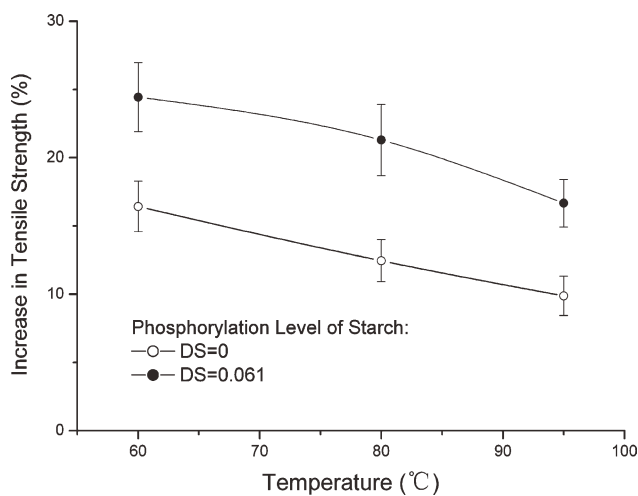


Figure 2. Increase in tensile strength of the wool yarns sized at different temperatures.

paste and possess the functions of jointing fibers together. It has been elucidated that internal stresses of adhesive layers are deleterious to an adhesion,²⁶ and toughening adhesive layers is extremely important to reduce the stresses.²⁷ When the layers consist of brittle materials like starch, the stresses are generally great, which is harmful to the adhesion. Apparently, the groups introduced and water absorbed supply plasticization for starch layers. Thus the modification enhances the adhesion of starch to wool fibers under lower temperature.

Effect on Mechanical Properties of Sized Wool Yarns

On the basis of the previous results achieved in our experiments, it is clear that phosphorylated starch possesses stable viscosity, weak retrogradation tendency, and strong adhesion to wool fibers in a range of 60–80°C when its modification level reaches the DS of 0.061. Further increasing the modification extent to 0.082 does not exhibit marked effect on above performances. For this reason, the phosphorylated starch with the

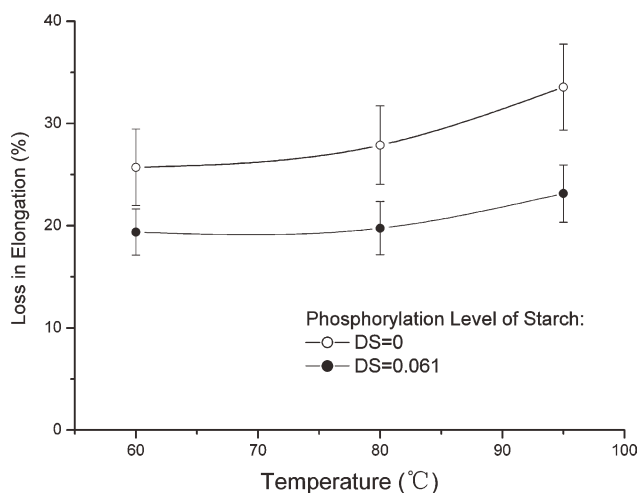


Figure 3. Loss in elongation of the wool yarns sized at different temperatures.

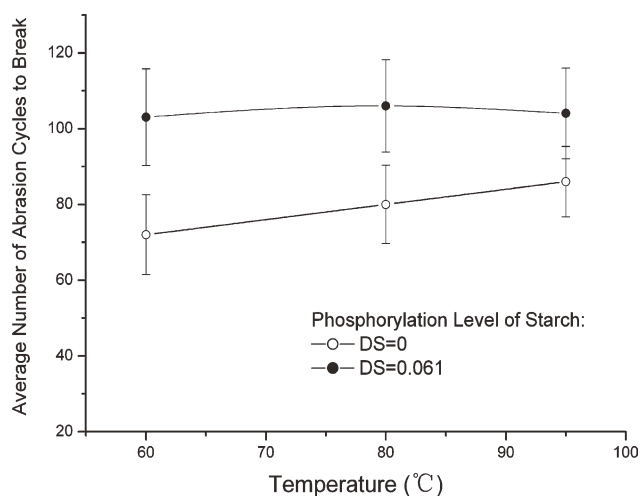


Figure 4. Average number of abrasion cycles of the wool yarns sized at different temperatures.

DS of 0.061 was used for the following sizing test so as to examine the effect of starch phosphorylation on sized wool yarns. Figures 2–4 describe the influences of phosphorylation and sizing temperature upon mechanical properties of sized wool yarns. Compared with the yarns sized with the non-phosphorylated starch (curve DS = 0), tensile strength and abrasion resistance of wool yarns sized with the phosphorylated starch increase, while the loss in elongation of the yarns decreases. The observation confirms that the quality of wool yarns sized with starch can be improved after starch has been phosphorylated. In addition, tensile strength and breaking elongation of the yarns sized under reduced temperature increase. Figure 4 indicates that abrasion resistance of the yarns sized with phosphorylated starch does not show much sensitivity to the variation of paste temperature. In contrast, the resistance of the yarns sized with the nonphosphorylated starch decreases as sizing temperature decreases. Apparently, improvement on the resistance is counteracted by the damage of wool yarns under high temperature. This result illustrates the importance to reduce the temperature during wool warp sizing. The observations demonstrate that mechanical properties of wool yarns sized with phosphorylated starch at 60–80°C can be greatly ameliorated when the modification level of starch reaches 0.061.

As is well known, a certain amount of fibers in sized yarns is adhered together by adhesion. Therefore, the strength of sized wool yarns is usually related to the adhesion. Increase in adhesion often results in increased yarn strength. On the other hand, wool yarns sized at reduced temperature is favorable to keep yarn elasticity and extension because fiber damages are reduced. Consequently, the loss in elongation is generally reduced under lower temperature after the yarns are pulled and stretched under moderate tension in wet region of sizing machine.

Starch film protects the yarns from mechanical abrasion by covering the yarn with a protective coating film of size.²⁸ Therefore, film behaviors should be considered for the evaluation of abrasion resistance of sized wool yarns. The effect of starch monophosphorylation on tensile behaviors of starch film is shown in

Table III. Effect of Starch Mono-Phosphorylation on Tensile Behaviors of Starch Film

Degree of substitution	Tensile strength		Breaking elongation		Work-to-break	
	S_t ($\text{N}\cdot\text{mm}^{-2}$)	CV (%)	E_b (%)	CV (%)	W_b ($\text{J}\cdot\text{mm}^{-2}$)	CV (%)
0	27.4	5.09	1.99	4.95	0.0234	9.76
0.021	27.5	5.22	2.23	11.32	0.0256	10.33
0.048	28.9	9.55	2.55	9.58	0.0383	10.28
0.061	30.8	7.40	2.75	8.77	0.0492	9.67
0.082	29.1	4.24	2.49	5.57	0.0338	8.16

CV expresses the coefficient of variation for the data in left column.

Table III. It can be observed that tensile strength, breaking elongation, and work-to-break of mono-phosphorylated starch film are evidently superior to those of hydrolyzed starch. They increase initially with the increase of DS value, reach maximum at DS = 0.061, and then decrease. It is evident that ionization of the phosphates introduced onto the backbones of starch in water occurs and forms negatively charged phosphates on starch molecules. The charged phosphates induce electrostatic charges and result in intermolecular repulsion. Obviously, the repulsion causes starch molecules extensive in aqueous paste and helps to bring about molecule entanglement during film-forming process, thereby initially enhancing tensile behaviors of the film. However, the phosphate groups introduced disturb association of adjacent hydroxyls and interfere with regular arrangement of starch molecules due to steric hindrance, which suggests a decreased trend to tensile strength. Therefore, a parabola variation was observed, and maximal strength occurred at the level of 0.061. Further increasing the level is inappropriate because of the declines in tensile behaviors of starch film. Furthermore, starch film is firmly connected by adhesion, thereby raising abrasion resistance. Since the phosphorylation enhances the adhesion and improves tensile behaviors of starch film, therefore, abrasion resistance of sized wool yarns is improved.

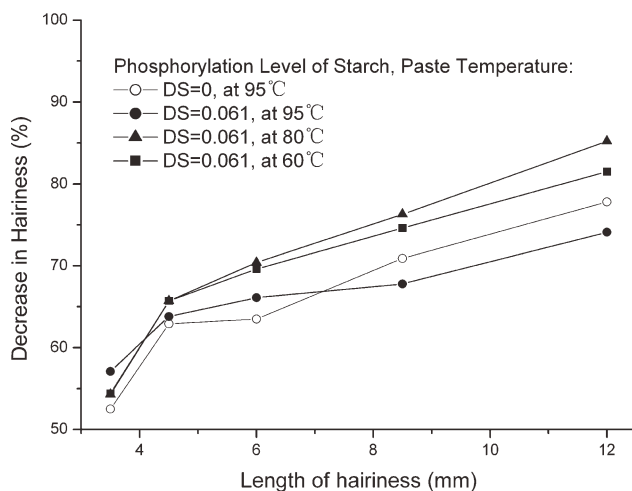


Figure 5. Effect of hairiness length on the decrease in hairiness of the wool yarns sized at different temperatures.

Effect on Hairiness of Sized Wool Yarns

Less hairy yarns are preferred since they often obtain better performance during weaving.^{29,30} Therefore, the influence of temperature variation upon the hairiness of sized wool yarns is evaluated. The hairs which are longer than 3 mm on surface of the yarns are depicted in term of decrease in hairiness at the length intervals in Figure 5. It can be seen that the hairs on the yarns sized with phosphorylated starch are related to the temperature. The decrease in hairiness is greater in value when the yarns are sized at either 80 or 60°C. This implies that lowering the temperature is favorable to reduce the hairiness. Obviously, reducing the temperature to such an extent can be realized with phosphorylated starch. And for native or hydrolyzed cornstarch pastes, they begin to gel if paste temperature is reduced to 60–80°C. However, it is surprising to find that the hairiness of the yarns sized at 95°C is similar no matter whether or not the starch is phosphorylated. As mentioned previously, mechanical properties of sized wool yarns decrease markedly after wool yarns have been sized under high temperature because wool fibers are very sensitive to hot water. The damage makes the fibers weaken, brittle, and lack of sufficient elasticity. In this case, fiber break occurs when sized yarns are separated by a force necessary to split the yarns at least rods. The broken fibers form new hairs on surface of sized yarns. Evidently, high temperature is deleterious to the decrease in hairiness of sized wool yarns. For this reason, lowering paste temperature is favorable to reduce the hairiness.

Assessment on Aerobic Biodegradation

Aerobic biodegradation of sizing agents in natural habitats is of considerable importance because a large quantity of sizing agents is used every year. Naturally, evaluation must be conducted to access the biodegradability of phosphorylated starch. Several studies^{31,32} had been performed on the biodegradability of sizing agents or related polymers. The investigators studied the biodegradability, as assessed by the BOD₅/COD ratio, to indicate their impact on environment. The ratio gives a gross index of the proportion of the organic materials present which are aerobically degradable within 5 days.³⁴ Therefore, the biodegradability of phosphorylated starch is assessed by measuring the BOD₅/COD ratio and comparing the ratios of phosphorylated starch with those of hydrolyzed one and synthetic materials related.

Table IV. Comparison on Individual BOD₅, COD, and BOD₅/COD Ratios of Some Sizing Agents Related to Wool Warps

Characterization	BOD ₅		COD		BOD ₅ /COD	
	Mean values (mg O ₂ L ⁻¹)	CV (%)	Mean values (mg O ₂ L ⁻¹)	CV (%)		
Hydrolyzed starch	DS = 0	35.0	13.9	114	7.51	0.307
Phosphorylated starch	DS = 0.021	33.0	10.8	103	8.63	0.320
	DS = 0.048	30.7	12.3	98.4	5.03	0.312
	DS = 0.061	29.2	10.2	94.1	7.22	0.310
	DS = 0.082	31.1	15.7	98.9	5.71	0.314
PVA	DP = 1700; DH = 99%	0.363	11.4	184	7.36	0.002
PEG	MW:1000	16.0	13.5	165	6.15	0.097
Bone glue	/	40.7	8.11	81.6	5.87	0.499

DP indicates the degree of polymerization; DH the degree of hydrolysis; and MW the molecular weights.

Table IV shows the comparison on individual BOD₅, COD, and BOD₅/COD ratios of hydrolyzed starch, phosphorylated starch, PVA, PEG, and bone glue. It can be seen that the ratios of hydrolyzed starch, phosphorylated one, and bone glue are much greater than those of PVA and PEG. The higher ratios of hydrolyzed starch, phosphorylated starch, and bone glue over the synthetics should be attributed to their high BOD₅ and low COD. For phosphorylated starch, the ratios are similar to the ones of hydrolyzed starch, and do not show much sensitivity to DS value. Obviously, aerobic biodegradation of phosphorylated starch is much better than that of PVA and PEG, and close to bone glue. As is well known, PVA causes problems in wastewater management due to high COD and low BOD.² Haines and Alexander³ confirmed that the rate and extent of PEG biodegradation decrease with the increase in chain length because higher molecular-weight PEGs are too large to penetrate bacterial cell. Therefore, the BOD₅/COD ratios of PEG and PVA are much lower than those of starches. This is most pronounced that phosphorylated starch is more easily biodegradable than PVA and PEG. Based on the data obtained in this investigation, aerobic biodegradation of phosphorylated starch is close to that of hydrolyzed one. Furthermore, the amount of phosphorus introduced onto backbones of starch is relatively lower. The modification level of DS = 0.061 corresponds to an increase of 1.12% in phosphorus content (vs. native starch, dry weight). Such a small phosphorus increment can be easily removed by means of wastewater treatment after desizing. In contrast, the improvement in sizing performances is significant for heat-sensitive wool yarns.

CONCLUSIONS

The results presented prove that mono-phosphorylation is an efficient way to improve the performance of cornstarch for sizing heat-sensitive wool yarns at reduced temperature. The phosphorylation impedes starch retrogradation under lower temperature, reduces temperature-sensitivity of starch paste, enhances the adhesion of starch to fiber substrates, and improves mechanical properties of starch film. In addition, the phosphorylation does not impeded aerobic biodegradation of

starch. These advantages and improvements supply a base for the phosphorylated starch to be used for sizing wool yarns under reduced temperature. Wool yarns sized with phosphorylated starch at 60–80°C still possess strong tensile strength, great elongation, high abrasion resistance, and lower hairiness. The advantages and improvements obtained also depend on the level of starch phosphorylation. Properly increasing the level of starch phosphorylation is capable of improving the end-use ability of starch mono-phosphate for sizing wool yarns under reduced temperature. However, excessively increasing the DS value is not preferred because of the reduction in tensile behaviors of starch film. Improvement on the quality of sized wool yarns can be achieved when the phosphorylated starch with a DS value of 0.061 are used as sizing materials. Monophosphorylation can be applied to improve the performance of cornstarch for sizing heat-sensitive wool yarns at 60–80°C.

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