Electroneutral quaternization and sulfosuccination of cornstarch for improving the properties of its low-temperature sizing to viscose yarns

Wei Li[a], Zhifeng Zhu, Xu Wang, Zhenzhen Xu & Xinhua Liu

College of Textiles and Garments, Anhui Polytechnic University, Wuhu 241000, China

The objective of this work is to evaluate the influences of electroneutral quaternization and sulfosuccination (electroneutral QS) on the adhesion of starch to viscose fibres and sizing properties of starch to viscose yarns at low temperature in order to study if the derivatization can improve the serviceability of starch applied for sizing viscose yarns at low temperature. The quaternized and sulfosuccinylated starch (QSS) with electroneutrality has been synthesized in aqueous dispersion by a quaternization of hydrolyzed cornstarch (HS) with N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride and a further sulfosuccination is done for introducing a fixed mole ratio of 3-(trimethylammonium chloride)-2-hydroxypropyl (TACHP) substituents to sulfosuccinate (SS) substituents onto starch chains. It is found that electroneutral QS is available to ameliorate the adhesion at different temperatures. The amelioration in the adhesion depends on the level of the modification. In addition, the modification improves the mechanical properties of the sized viscose yarns, and decreases hairiness of sized yarns, even if the temperature of the electroneutral QSS paste is lowered to 60 °C. Electroneutral QSS with a degree of substitution of 0.0438 is expected to show a potential application in sizing viscose yarns at 60 °C.

Keywords: Cornstarch, Electroneutral quaternization and sulfosuccination, Sizing properties, Viscose yarns

1 Introduction

Obviously, the paste temperature in size box depends upon the type of fibres and the nature of sizes during warp sizing process. According to the difference in paste temperature, warp sizing can be divided into high- and low-temperature sizing for staple fibres. The temperature above 95 °C is described as high-temperature sizing, and that below 80 °C is known as low-temperature sizing[1].

Starch has many advantages like abundant resources, low price, environment friendliness, and relatively strong adhesion to fibres[2]. A great deal of starch is applied for warp sizing and paper making. Starch has become a sizing agent that possesses the largest usage in warp sizing. Accordingly, the development of starch sizes is particularly important for sizing warps. Usually, when a starch-based sizing agent is used in size formulation for sizing warps, paste temperature in size box is kept at 95-99 °C (ref. 3). As a result, there is a lot of steam energy consumed for maintaining the temperature throughout the entire sizing operation[4]. Undoubtedly, the energy consumed in warp sizing will be saved if paste temperature can be reduced. However, native starch paste has the gelling tendency[2] at low temperature. The gelling is mainly attributed to the retrogradation or microcrystallization generated by the re-association of starch hydroxyls between amyloses[5]. After gelling, the starch paste will lose the liquidity, form a rigid interlocked chain structure, and become an irreversible gel having 3-dimensional network held together by hydrogen bonding[6,7]. It cannot be effectively handled for sizing purposes as the gelled starch paste is used. Hence, starch paste must be used at high temperature throughout the entire sizing operation[8]. Also, starch cannot satisfy sizing requirement of heat-sensitive fibres like viscose fibres. The reason is attributed to its greatly reduced strength when viscose yarns are subjected to high-temperature sizing at above 85 °C (ref. 9). Consequently, sized viscose warp property, loom efficiency, and fabric quality will be negatively influenced. For these reasons, there is an urgent need to alleviate the gelling tendency of starch paste at low temperature for meeting the requirements of low-temperature sizing of viscose warps and saving the energy.

Apparently, strong adhesion to fibres can be considered as an extremely important characteristic

_____
[a]Corresponding author.
E-mail: fangzhiliweiwu@sina.com

for every kind of sizing agents[10]. The adhesion is able to promote the strength of the yarns by gluing the fibres in warp yarns together[11]. It is also capable of decreasing yarn hairiness through adhering to the hairs onto the yarn body[10]. As a result, the characteristic is closely correlated with the quality of sized warps[12, 13], and determines the size pick-up that a warp yarn must be sized[11]. Therefore, the adhesion has been widely studied in recent years[14, 15]. In addition, it is well important to emphasize that cellulosic fibres such as viscose fibres have negative charges in water[16, 17]. Accordingly, positively charged substituents derivatized onto the backbones of starch can improve the adhesion via generating electrostatic attraction with cellulosic fibres at starch adhesive layer-fibre interfaces[18]. Nevertheless, positively charged substituents disfavor the desizability of starch owing to the attraction[19]. It is undoubted that the introduction of negatively charged substituents onto the starch chains will show adverse effect on the adhesion due to the electrostatic repulsion between negatively charged substituents and cellulosic fibres. Our previous work[20] has demonstrated that amphoteric modification with electroneutrality performed via introduction of positively charged 3-(trimethylammonium chloride)-2-hydroxypropyl (TACHP) substituents and negatively charged sulfosuccinate (SS) ones onto the starch chains simultaneously not only has strong adhesion to viscose fibres, but also has good desizability. The TACHP and SS substituents have large volume, and hence it is imagined that the steric hindrance of the two substituents introduced may interfere with the association of amyloses and diminish the retrogradation or gelling tendency of cold starch paste. Accordingly, electroneutral quaternization and sulfosuccination (electroneutral QS) of starch may be expected to improve the adhesion of starch paste to viscose fibres at low temperature. Currently, little has been known about the impact of electroneutral QS on the adhesion of starch to fibres at low temperature. Also, to the best of our knowledge there are no studies available on the effect of electroneutral QS of starch on the properties of low-temperature sizing of viscose yarns. Therefore, the objectives of this research are to reveal if electroneutral QS is able to improve the adhesion and enhance the serviceability of starch sizes used in low-temperature sizing of viscose wraps via eliminating the shortcomings of native cornstarch such as the gelling tendency of the starch paste at low temperature, etc.

2 Materials and Methods

2.1 Materials

Native cornstarch with an apparent viscosity of 53 mPa·s was purchased from Yixing Starch Factory (Jiangsu Province, China). The starch was refined to remove the protein components[21], and then hydrolyzed[3] with HCl to decrease its excessive viscosity before performing derivatization of the starch.

The cationic etherifying agent N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride [CHPTAC, an active principle of 50 % (w/w)] was an industrial product and obtained from Yinhu Chemical Co. Ltd. (Zhejiang, China). Maleic anhydride and sodium bisulfite were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All other chemicals, obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), were of analytical grade and used as received without further purification.

Pure viscose roving (590 tex linear density and 52 twist factor) used as substrate for adhesion measurement was offered by Tianyi Textile Co. Ltd. (Jiangsu, China). The average length and fineness of viscose fibres in the roving were 38 mm and 1.33 dtex respectively. Pure viscose yarns (ring-spun, 14.8 tex) used in sizing measurement were obtained from Chunjiang Textile Group Co. Ltd. (Zhejiang, China).

2.2 Modification of Starch

Hydrolyzed starch (HS) was exposed to quaternization and sulfosuccination for synthesizing electroneutral QSS. The sulfosuccination includes maleation and sulfonation. Therefore, electroneutral QSS was prepared via quaternization of HS with CHPTAC, then maleation with maleic anhydride, and further sulfonation with sodium bisulfite.

Starch quaternization was carried out in aqueous suspension by reacting granular HS with cationic etherifying agent (CHPTAC) for introducing TACHP groups. The 40 % (w/w) aqueous suspension (324 g dried HS suspended in 486 mL distilled water containing 32g anhydrous sodium sulfate) was transferred into a three-neck round flask equipped with a mechanical stirrer. Then, the suspension was adjusted at *p*H 10-11 using 3 % (w/w) NaOH solution and heated up to 40 °C. Thereafter, mixture solution (containing equal mole of CHPTAC and NaOH) was dropped into the suspension through the dropping funnel. Ten minutes later, calcium oxide aqueous solution (0.067 g/mL) was added. The cationic etherifying reaction was subsequently conducted at above temperature under mechanical stirring for 8 h.

Finally, the reaction product was neutralized (pH 6.5-7), filtered, and re-suspended for performing maleation of starch sample with maleic anhydride.

Firstly, pH of the resuspension (40 %, mass fraction) was adjusted to 8-9 using 6 % (w/w) Na_2CO_3, and its temperature was raised to 30 °C in water bath with continuous stirring. Then, a definite amount of maleic anhydride acetone solution (30 %, by wt) was dropped into the resuspension, using the Na_2CO_3 solution to maintain the pH at 8-9. Afterwards, the starch product was neutralized to pH 6.5-7, and vacuum-filtered. Finally, the product was re-suspended in distilled water (containing excessive amount of sodium bisulfite) to form 35 % (w/w) resuspension for carrying out the following sulfonation.

The sulfonation was performed at 40 °C in water bath for 5 h under mechanical agitation. Afterwards, pH of the reaction product was neutralized to approximately 7 using Na_2CO_3 solution, dewatered by washing thoroughly with ethanol, vacuum-filtered, dried in a vacuum oven at 40 °C, milled into powder, and sieved with a 100-mesh sieve.

2.3 Characterization of Amphoteric Starch Derivative

Its quaternization level [degree of substitution of TACHP substituents (D_c)] was calculated through following Eq. (1) according to the nitrogen content measured using the Kjeldahl method[22]. The efficiency of the quaternization $(E_c, \%)$ was calculated according to the following Eq. (2):

$$D_c = \frac{162N}{14 \times 100 - 151.5N} \qquad \ldots (1)$$

$$E_c = \frac{D_c \times m_0}{m_1} \times 100\% \qquad \ldots (2)$$

where N is the nitrogen contents (%, by wt); 162, 14 and 151.5, the molecular weights of anhydroglucose units (AGU), molecular weight of nitrogen, and difference between molecular weight of the TACHP substituents introduced and one of hydrogen atom respectively; and m_0 (mol) & m_1 (mol), the molar quantities of AGU and CHPTAC charged respectively.

Titrimetric analysis[23] based on the principle of Br addition was used as a control to titrate the double bonds in maleinates introduced. The maleation level (D_m) and its efficiency $(E_m, \%)$ were calculated using the following equations:

$$y = \frac{(V_0 - V_1) \times C \times 0.0799}{W} \times 100\% \qquad \ldots (3)$$

$$D_m = \frac{162y}{79.904 \times (2 - 1.214y)} \qquad \ldots (4)$$

$$E_m = \frac{D_m}{m_2/m_0} \times 100\% \qquad \ldots (5)$$

where y (%) is the bromine value of quaternized and maleated starch product; V_0 (mL) & V_1 (mL), the volumes of standard $Na_2S_2O_3$ solution consumed in blank and the modified starch titration respectively; C (mol/L), the concentration of standard sodium hyposulfite solution; W (g), the weight (dry basis) of the modified starch; 79.904, the atomic weight of bromine; and m_2 (mol), the molar quantity of maleic anhydride charged.

The efficiency of sulfonation $(E_s, \%)$ and its level (D_s) was determined based on the principle of Br addition to double bonds in the substituents and calculated according to the following equations:

$$E_s = \frac{y_0 - y_1}{y_0} \times 100\% \qquad \ldots (6)$$

$$D_s = \frac{y_0 - y_1}{y_0} \times D_m \qquad \ldots (7)$$

where y_0 (%) & y_1 (%) are the bromine values of starch samples before and after sulfonation respectively.

2.4 Zeta Potential of Paste

Zeta potential measurements of cooked starch pastes were conducted on a Malvern Zetasizer Nano-ZS90 (Malvern Instrument Inc., Worcestershire, UK) according to the method reported earlier[20].

2.5 Adhesion to Viscose Fibres

In this work, the method of roving sizing[24] was employed to access the adhesion of starch paste to viscose fibres in accordance with FZ/T 15001-2008 except the paste temperature. Briefly, starch pastes were prepared by weighing starch and adding water to form an aqueous dispersion (1.0 %, by wt.) followed by continuous heating and stirring for 1 h at 95 °C. The pastes were cooled up to requisite temperatures (80 °C, 60 °C, and 25 °C respectively) and kept at these temperatures for 4 h with continuous stirring before adhesion measurement. Thereafter, the viscose

roving, carefully wound onto a stainless steel frame, was impregnated with the pastes for 5 min. The frame was hung for drying the sized roving in air. After having been kept at 65 % RH and 20 °C for 24 h, the tensile strength of dry sized roving was determined on an HD026NS Electronic Strength Tester (Nantong Hongda Experimental Instrument Co. Ltd., Jiangsu, China) with an initial chuck-distance of 100 mm and a drawing speed of 50 mm/min. For every sample, the result reported was the average of 20 individual tests.

2.6 Light Transmittance of Starch Paste

Light transmittance of starch paste was measured using an UV9600 spectrophotometer (Ruili Analytical Instrument Co., Ltd., Beijing, China) against distilled water blank according to the method of Craig[25] at 640 nm (ref. 26).

2.7 Moisture Adsorption of Starch Film

Moisture adsorption (%) of the film was determined by measuring weight loss of starch film upon drying to constant weight in an oven at 105 °C according to the literature[27]. Moisture adsorption was determined in duplicate and calculated using the following equation:

$$\text{Moisture adsorption} = \frac{M_0 - M_1}{M_1} \times 100\% \qquad \dots (8)$$

where M_0 and M_1 are the wet and dry weights of the film pieces respectively.

2.8 Sizing Procedure

To estimate the serviceability of electroneutral QSS in sizing viscose yarns at low temperature, a GA392 Miniature Sizing Machine (Tongyuan Textile Machinery Co. Ltd., Jiangyin, China) was employed to size viscose yarns at a speed of 20 m/min. The yarns were impregnated with the paste at 95° ± 2 °C for performing high-temperature sizing or at 60° ± 2 °C for low-temperature sizing. Subsequently, the sized yarns were wound onto a small bobbin.

2.9 Measurement on Sizing Properties

Size pick-up of the sized viscose yarns was determined according to the literature[28]. Tensile strength and extension-at-break of the sized yarns were determined on a HD021E+ Tensile Tester (Nantong Hongda Instrument Co. Ltd., Jiangsu, China) at 65 % RH and 20 °C with a drawing speed of 500 mm/min, test length of 500 mm and an initial tension of 7.3 N. For each sample, the increase in tensile strength and the loss in the extension respectively were calculated using the following equations:

$$\text{Increase in tensile strength} = \frac{N - N_0}{N_0} \times 100\% \qquad \dots (9)$$

$$\text{Loss in extension} = \frac{E - E_0}{E} \times 100\% \qquad \dots (10)$$

where N & N_0 are the mean tensile strengths of the sized and unsized (raw) viscose yarns respectively; and E & E_0, the mean extensions of the raw yarns and sized ones respectively.

A LFY-109B Computer Yarn Abrasion Tester (Textile Science Research Institute, Shandong, China) was used to measure the abrasion resistance of sized yarns at above condition with a preliminary weight of 5 g per end of the yarns. The data reported were the average abrasion cycles to break the yarns for 20 successful specimens.

Hairs existed on warp surfaces were investigated by measuring the percentage of hairs bonded onto the body of yarns, i.e. decrease in hairiness (%). Hairiness was measured using an YG173 Hairiness Tester (Changling Textile Electromechanical Factory, Shanxi, China) at a moving speed of 10 m/min. The tester counts the number of hairs that are longer than 3 mm in each 5 m section, and records 10 times for each sample. Decrease in hairiness was calculated as shown below:

$$\text{Decrease in hairiness} = \frac{S_1 - S_0}{S_1} \times 100\% \qquad \dots (11)$$

where S_1 & S_0 are the mean values of hairiness on raw and sized viscose yarns for measuring 10 times respectively.

In order to observe the amount of hairs on yarn surfaces, Scanning Electron Microscopy (SEM) imaging was conducted on the raw and sized yarn surfaces using FEI Quanta-200 Scanning Electron Microscopy (FEI Company, Holland) operated at 5 kV. Prior to observation, the yarn surfaces were coated with a thin gold layer.

3 Results and Discussion

3.1 Electroneutral QSS Analysis

In this investigation, cornstarch was cationically and anionically modified simultaneously in aqueous suspension as depicted in Fig. 1. Figure 1(a) corresponds
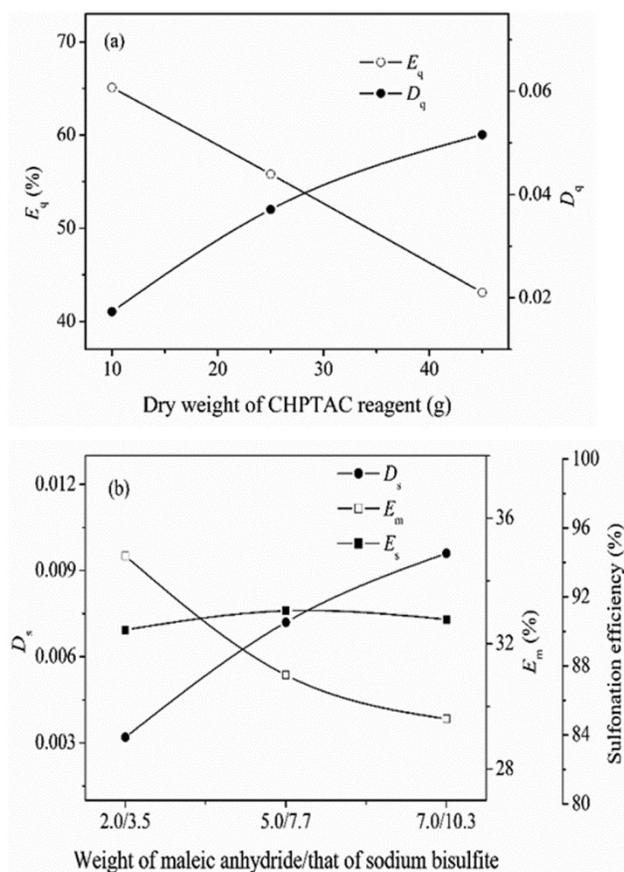
Fig. 1 — Characterization of the electroneutral QSS samples prepared

Fig. 2 — Zeta potentials of electroneutral QSS samples prepared with different total degrees of substitution

to starch quaternization with CHPTAC for introducing positively charged TACHP substituents, while sulfosuccination (Fig. 1(b)) containing maleation with maleic anhydride and sulfonation with sodium bisulfite. As observed, with the increase in the amounts of CHATAC reagent and maleic anhydride to starch, reaction efficiencies (E_q) of CHATAC reagent and ones (E_m) of maleic anhydride were gradually decreased, in contrast, degrees of substitution of quaternization and maleation increased continuously. In addition, it can be found from Fig. 1(b) that sulfonation efficiencies are all above 90 %. characterization of (a) starch quaternization and (b) further sulfosuccination

Obviously, increasing the amounts of CHATAC and maleic anhydride reagents to starch can provide adequate CHATAC and maleic anhydride molecules for reacting with free hydroxyl groups of starch granular surfaces as well as raise their concentrations in the suspension, favoring a promoting effect to the modification reaction, thereby leading to a gradually increased modification level. However, as the reaction
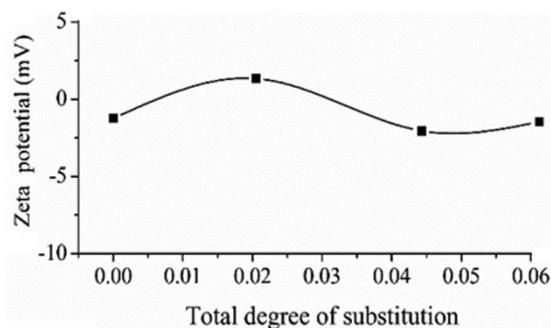
goes on, there are not enough free hydroxyl groups on starch granular surfaces for introducing new TACHP groups and maleates onto the backbones of starch, thereby lowering the reaction efficiencies of quaternization and maleation and resulting in a gradually decreased reaction efficiencies as the amounts of CHPTAC and maleic anhydride increase.

To confirm the electroneutrality feature of QSS prepared, the zeta potential of cooked QSS paste is conducted and the measurement results are shown in Fig. 2. It can be found that zeta potentials of the QSS samples prepared are all approximately 0 mV. This indicates that QSS samples prepared in this research by starch quaternization and sulfosuccination in aqueous suspension are electroneutral.

3.2 Influence of Electroneutral QS on Adhesion-to-Viscose Fibres at Low Temperature

3.2.1 Influence of Electroneutral QS Level

When sizing temperature is above 85 °C, tensile strength of viscose fibres rapidly reduces[9]. Therefore, sizing of viscose warps is commonly performed at <85 °C. In this investigation, adhesion of electroneutral QSS to viscose fibres estimated by the measurement of tensile strength of sized viscose roving is determined at 95 °C and 80 °C for revealing if the electroneutral QS can improve the adhesion of starch to viscose fibres with no damage to viscose fibres (Table 1). It can be found that tensile strength of viscose roving sized with cooked electroneutral QSS paste is apparently higher than that sized with cooked unmodified starch paste. This means that electroneutral QS can obviously ameliorate the adhesion of starch to viscose fibres. Moreover, as observed, tensile strength is relied on electroneutral QS level, and irrespective of temperature applied, the tensile strength gradually increases as the electroneutral QS level is increased. After starch electroneutral QS, the difference in tensile strengths

Table 1 — Influence of electroneutral QS level on the adhesion

Starch samples	Electroneutral QS levels	Tensile strength $\times 10^{-3}$ N/tex	
		95°C	80°C
HS	0	145±9.2	140±8.4
Electroneutral	0.0205	157±9.0	153±8.5
QSS	0.0433	165±8.1	163±7.7
	0.0612	170±9.2	169±9.2

Fig. 3 — Moisture adsorption of films

of sized viscose roving impregnated with the electroneutral QSS pastes at 80 °C and at 95 °C is less than that of unmodified cornstarch. This indicates that the electroneutral QSS would be a good adhesive that can be applied for sizing viscose yarns at about 80 °C, thereby favoring to reduce the damage on viscose fibre due to high temperature and to promote the serviceability of starch in viscose warp sizing.

As is well known, starch consists of two major polymers, namely: linear amylose and branched amylopectin[29]. Cooked natural starch paste can be considered as a biphasic system that causes swelling in fragments dispersed in a continuous phase[30, 31]. The fragments dispersed in the paste consist of branched amylopectin while the linear amyloses can dissolve in aqueous phase during heat-induced pasting. Linear amylose chains in cooked starch aqueous paste have a tendency of parallel arrangement with each other and form hydrogen bonds between hydroxyls. This phenomenon of intermolecular association between amylose chains is commonly known as retrogradation[32]. At a high concentration, the retrogradation makes the starch paste convert into a gel that is made up of three-dimentional network held together through hydrogen bonding[32]. Apparently, a gelled starch paste losses its liquidity and cannot wet and spread sufficiently onto the fibre surfaces. In addition, due to the existence of the fragments, the paste becomes microheterogeneous, inevitably resulting in incomplete wetting and spreading of starch paste at fibre surfaces. Insufficient and incomplete wetting and spreading can lead to interfacial defects around outspreaded and/or unwetted areas. Moreover, starch paste distributed among the fibres shrinks in volume due to evaporation of water during drying, and then forms adhesive layers between fibres for gluing them together. The shrinkage during formation of adhesive layers generates internal stresses at the interfaces and within matrices of the layers[7]. As elucidated, incomplete wetting, outspreading and internal stresses induced are harmful to adhesion[33]. Consequently,
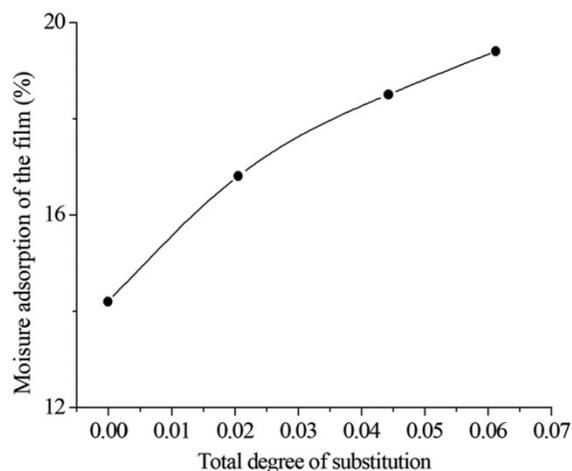
native starch commonly exhibits low adhesion to fibres at high and low temperatures.

Nevertheless, through starch derivatization (electroneutral QS), certain amounts of TACHP and SS substituents are derivatized onto starch chains. The two substituents are able to store water within starch adhesive layers due to their characteristic of absorbing water, such as their hydrophilicity. The water content stored within starch adhesive layers can be estimated by the measurement of moisture adsorption of the films (Fig. 3). It can be found that moisture adsorption of electroneutral QSS film is higher than that of HS film. Water is an effective plasticizer[34, 35] to starch matrices. Therefore, the substituents introduced are beneficial in reduction of the stresses and stress concentration both at bonded interfaces and within starch adhesive layers. Moreover, the substituents with large space volume make them to exhibit strong steric hindrance. Owing to the hindrance the substituents are able to interfere with the regular arrangements of linear amyloses during the formation of adhesive layers from cooked starch paste. As a result, the increased hydrophilicity and hindrance favor to promote water-dispersibility of starch molecules in continuous phase. A starch paste with great water-dispersibility is expected to improve wetting and spreading of the paste at fibre surfaces and reduce interfacial defects. Obviously, steric hindrance of the substituents can also produce toughening effect on starch adhesive layers, thereby reducing the stresses and their concentration. Consequently, the substituents introduced diminish probabilities of cohesive and interfacial failures, thereby ameliorating the adhesion of starch to viscose fibres. And these positive effect factors strengthen

with the increase in the electroneutral QS. As a result, a gradually ameliorated adhesion is displayed as the electroneutral QS level rises.

Furthermore, in order to elucidate the reason that electroneutral QS can improve the adhesion of starch to viscose fibres at 80 °C, the gelling tendency of the paste due to the paste retrogradation must be considered. The gelling tendency of the paste can be evaluated by the variations in light transmittances of starch pastes, as practically examined by Sangseethong *et al*[36]. The transmittances of cooked HS and electroneutral QSS pastes maintained at different temperatures for 3 h are shown in Fig. 4. The figure indicates that the decrease in the transmittance of electroneutral QSS pastes from temperature 95 °C to 80 °C is small as compared to that of HS paste. It is also observed that with the increase in level of electroneutral QS, the decrement in the transmittance of electroneutral QSS pastes shows a continuous reducing tendency. The observation suggests that the electroneutral QS is able to alleviate the gelling tendency of the starch paste, and the alleviation strengthens as the modification level increases. The reason of the alleviation in gelling tendency produced by the electroneutral QS is mainly attributed to steric hindrance of TACHP and SS substituents introduced. The steric hindrance of the substituents causes a resistance to the retrogradation of the paste owing to the disturbance in the re-association of starch hydroxyls and the obstruction in the regular arrangement of amyloses, consequently reducing the gelling tendency of the starch pastes at 80 °C. Therefore, the factors for improving the adhesion of starch to viscose fibres at 80 °C are attributed to the plasticization and increased water-dispersibility arisen from the hydrophilicity & steric hindrance of the substituents, and alleviation of gelling tendency of the starch paste. The increase in the hydrophilicity and steric hindrance as well as the enhancement in the alleviation result in the gradual improvement in adhesion as the modification level increases. Additionally, the differences in tensile strengths of viscose roving sized with unmodified or modified starch paste at 95 °C and 80 °C are low. It may be due to the damage on viscose fibres at high temperature. The damage reduces the strength of viscose fibres in hot water. And when the temperature is below 85 °C, the damage at high temperature to viscose fibres rapidly reduces. As a result, a slight difference in the adhesion is shown. However, electroneutral QS can alleviate the gelling tendency of the starch paste,
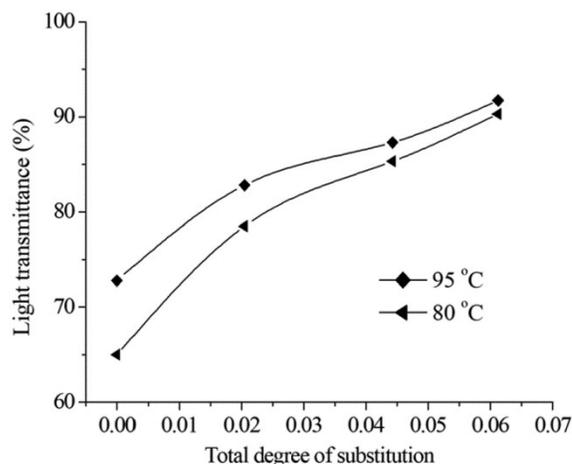

Fig. 4 — Influence of total degrees of substitution on light transmittance of cooked electroneutral QSS pastes
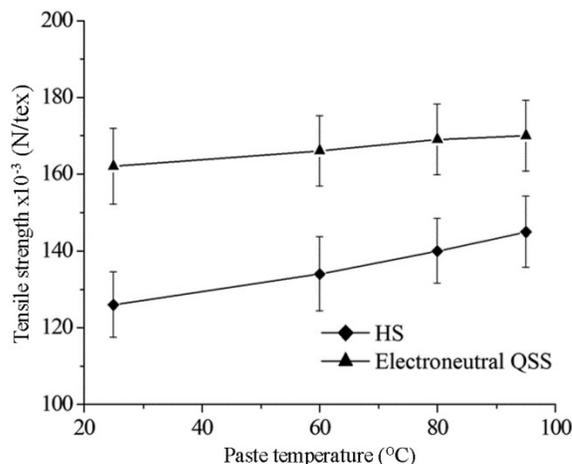

Fig. 5 — Influence of paste temperature on adhesion of starch to viscose fibres

thereby lowering the negative effect of gelling tendency on the adhesion. Therefore, the difference in the adhesion result for electroneutral QSS is smaller than that for HS.

3.2.2 Influence of Paste Temperature

Influence of paste temperature on the adhesion of starch to viscose fibres is evaluated and shown in Fig. 5. Irrespective of paste temperature, tensile strength of viscose roving sized with cooked electroneutral QSS paste is superior to that sized with the HS paste. This implies that electroneutral QS can promote the adhesion at low temperature.

Besides the plasticization produced by the hydrophilicity and steric hindrance of the substituents, the alleviation of gelling tendency of the starch paste after starch electroneutral QS can be considered as the principal influence factor. The alleviation in gelling

tendency is mainly due to the steric hindrance of the two substituents introduced. The hindrance is able to disturb hydrogen bond association among starch hydroxyls, reduces the amount of hydrogen bonds among starch chains, and interfere with regular arrangement of starch amyloses, thereby diminishing the retrogradation of starch paste and alleviating its gelling tendency. A reduced gelling tendency favors to raise liquidity of starch paste, thus improving the wetting and spreading of the paste at fibre surfaces. Consequently, electroneutral QS is capable of improving the adhesion of starch to viscose fibres at low temperature.

3.3 Sizing Properties of Electroneutral QSS to Viscose Yarns

Based on the previous data, electroneutral QSS with a DS value of 0.0433 has lower paste retrogradation, and strong adhesion to viscose fibres at 60 °C. Additionally, the increase in DS value is further limited owing to lower reaction efficiency of electroneutral QS, which can also raise the cost of synthesis. Therefore, the electroneutral QSS prepared with the DS value of 0.0438 is applied for sizing viscose yarns at 93 °C and 60 °C to investigate its serviceability in sizing the yarns at low temperature.

Table 2 presents a comparison of electroneutral QSS with HS on tensile properties and abrasion resistance of sized viscose yarns. Compared to the yarns sized with HS at 93 °C, the increase in tensile strengths and abrasion resistance of the yarns sized with electroneutral QSS both at 93 °C and 60 °C are greater, whereas the losses in elongations are lower. This observation reflects that the quality of viscose yarns sized with electroneutral QSS is superior to that sized with HS. In addition, tensile strength, breaking elongation, and abrasion resistance of the yarns sized with electroneutral QSS do not show much sensitivity to paste temperature. This infers that the quality of the sized yarns does not remarkably depend on sizing temperature when electroneutral QSS is applied. During warp sizing, the increase in the strength is achieved due to the adhesion of a sizing agent to fibres in the yarns, i.e. by adhering to the fibres

together. Generally, the better the adhesion, the stronger is the strength of sized yarns. Previous experimental result of adhesion measurement indicates that the adhesion of electroneutral QSS to viscose fibres at 95-60 °C is greater than that of HS at 95 °C. Accordingly, electroneutral QSS is superior to HS in increasing yarn strength.

When electroneutral QSS is used, the TACHP and SS substituents introduced can disturb starch arrangement due to their steric hindrance. In addition, the hydrophilic substituents are capable of absorbing water. The steric hindrance and the water absorbed lower the brittleness of starch adhesive layers, which is rather important to relax the stresses developed at the interfaces between the layers and the fibres in the yarns as well as within the layers. For this reason, the loss in the elongation of viscose yarns sized with electroneutral QSS is smaller than that sized with HS.

The steric effect and absorbed water provide the toughening effect for starch adhesive films formed at yarn surfaces and enhance their flexibility, thereby decreasing the internal stresses. Moreover, the modification reduces gelling tendency of the starch paste, which results in the decreased defects of the films on surface of yarns. The films with lower stresses and fewer defects can better protect the yarns from abrasion. In this case, abrasion resistance of the viscose yarns sized with electroneutral QSS increases.

Furthermore, weaving efficiency is directly correlated with the hairiness on the surfaces of sized yarns, particularly for air-jet weaving machines. The yarns with fewer hairs are preferred since they often have better weaving ability[37]. Accordingly, the influence of starch modification on hairiness of the yarns sized at low temperature should be investigated in terms of decrease in hairiness (%), as also shown in Table 2. As observed, the hairiness of the yarns sized with electroneutral QSS is lower than those sized with HS. Surprisingly a decrease in paste temperature does not result in great increase in hairiness when electroneutral QSS is applied. It is well known that the hairiness of sized yarns depends on the adhesion.

Table 2 — Influence of electroneutral QS on mechanical properties[a] and hairiness[b] of sized viscose yarns

Starch samples	Sizing temperature °C	Size add-on %	Increase in tensile strength, %	Loss in elongation, %	Abrasion resistance cycles	Decrease in hairiness %
HS	93	11.4	14.7	28.9	724	83.6
Electroneutral QSS	93	10.2	17.4	22.2	958	93.4
	60	9.51	16.8	21.3	872	91.1

[a] Tensile strength, breaking elongation and abrasion resistance of raw viscose yarns are 12.4 cN/tex, 11.4 % and 89 cycles respectively.
[b] The Number of hairs with a length of $\geq$ 3 mm in per 5 m of the raw viscose yarns is 53.5.
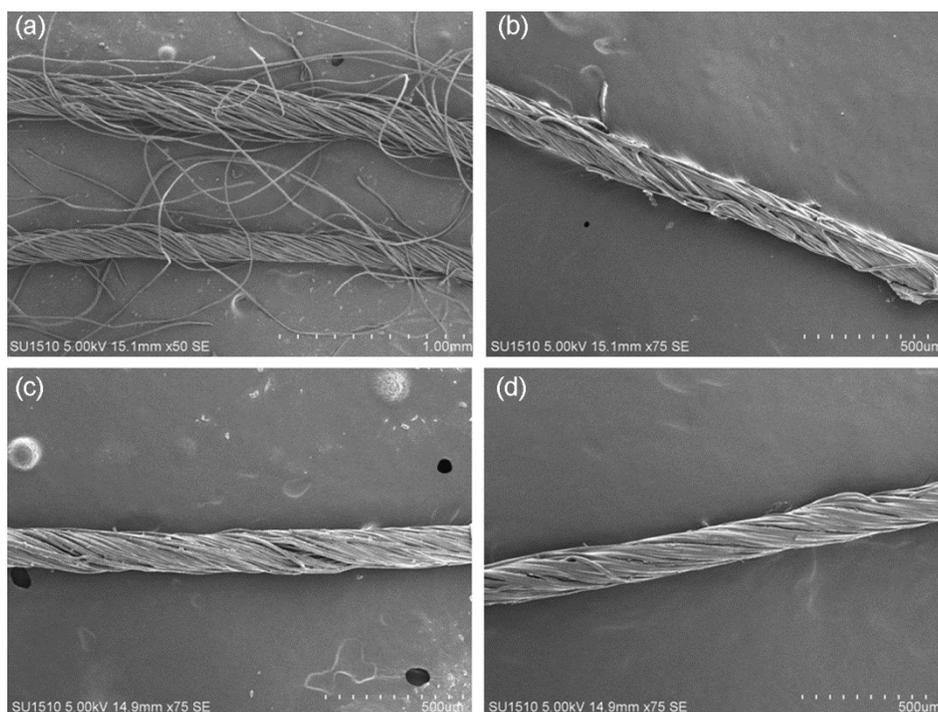
Fig. 6 — SEM images of raw viscose yarns (a), and sized viscose yarns: (b) sized at 93 °C with HS paste, (c) sized at 93 °C with electroneutral QSS paste, and (d) sized at 60 °C with electroneutral QSS paste

The better the adhesion, the lower is the hairiness of sized yarns. The data obtained above indicates that electroneutral QS is able to enhance the adhesion, thereby reducing hairiness of the sized yarns at low temperature. Additionally, hairiness of the sized yarns can be observed by conducting scanning imaging on the yarn samples. SEM images of the samples are presented in Fig. 6. It can be seen that there are a large number of hairs on the surface of raw viscose yarns, whereas a fewer hairs exist on the surface of sized yarns. This observation suggests that it can remarkably reduce the hairiness by performing the sizing process to the raw viscose yarns. During warp sizing, the starch paste glues the hairs back onto the body of the yarns by its own adhesion, producing an efficient effect of covering hairiness. As a result, the hairiness is significantly reduced by sizing the viscose yarns.

4 Conclusion

Electroneutral quaternization and sulfosuccination is found to be an efficient method to improve the properties of corn starch for sizing viscose warp yarns at low temperature. The modification increases the adhesion of starch to viscose fibres, and an increased tensile strength is observed as the total DS value raises. This increase supplies a base for electroneutral QSS to be used as warp sizing agents.

The electroneutral QSS with a suitable DS value of 0.0438 can be applied to improve the sizing properties at 93 °C, and the warps sized with electroneutral QSS exhibit the stronger tensile strength, greater extension, higher abrasion resistance, and fewer hairs than those sized with HS. Furthermore, the warps sized with electroneutral QSS at 60 °C still possess strong tensile strength, great elongation, and high abrasion resistance. It displays potential application in low-temperature sizing of viscose warps at 60 °C.

References
1 Xu D S, *Theory of Weaving (in Chinese)* (China Textile and Apparel Press, Beijing, China), 2008, 72-132.
2 Goswami B C, Anandjiwala R D & Hall D M, *Textile Sizing* (Marcel Dekker, New York • Basel), 2004, 135-200 & 201-272.

3   Zhu Z F, Liu Z J, Li M L, Xu D S & Li C L, *J Appl Polym Sci*, 127(2013) 127.
4   Tong Y, *Appl Mech Mater*, 508(2014) 223.
5   Zhou Y Y, *Theory of Textile Warp Sizes (in Chinese)* (China Textile and Apparel Press, Beijing, China), 2004, 115-260.
6   Behera B K & Gupta R, *J Appl Polym Sci*, 109(2008) 1076.
7   Zhu Z F & Wang M, *J Adhes Sci Technol*, 28(2014) 935.
8   Moreau J P, *Text Chem Color*, 13(1981) 22.
9   Zhu Z F & Liu Z J, *Starch-Stärke*, 61(2009) 139.
10 Zhu Z F & Chen P H, *J Appl Polym Sci*, 106(2007) 2763.
11 Trauter J, Vialon R & Stegmeier T, *Melliand Eng*, 72(1991) 251.
12 Zhu Z F & Cheng Z Q, *Starch-Stärke*, 60(2008) 315.
13 Zhu Z F & Zhuo R X, *J China Text Univ (Eng Ed)*, 14(1997) 43.
14 Qiao Z Y, Zhu Z F & Wang Q, *AATCC Rev*, 11(2011) 65.
15 Yang S Y & Huang C Y, *J Appl Polym Sci*, 109(2008) 2452.
16 Shi W X, Xu X J & Sun G, *J Appl Polym Sci*, 71(1999) 1841.
17 Grancaric A M, Tarbuk A & Pusic T, *Color Technol*, 121(2005) 221.
18 Zhu Z F & Lei Y, *J Adhes Sci Technol*, 29(2015) 116.
19 Zhu Z F & Shen S Q, *J Adhes Sci Technol*, 28(2014) 1695.
20 Li W & Zhu Z F, *J Adhesion*, 92(2016) 257.
21 Zhu Z F & Zhuo R X, *Eur Polym J*, 37(2001) 1913.
22 Olusola A J, Adebiyi O B & Riyaad K, *Starch-Stärke*, 67(2015) 561.
23 Zhu Z F, Zhang L Q, Li M L & Zhou Y S, *Starch-Stärke*, 64(2012) 704.
24 Jin E Q, Zhu Z F, Yang Y Q, Miao G C & Li M L, *J Text Inst*, 102(2011) 681.
25 Craig S A S, Maningat C C, Seib P A & Hoseney RC, *Cereal Chem*, 66(1989) 173.
26 Sandhu K S, Singh N & Lim S T, *LWT-Food Sci Technol*, 40(2007) 1527.
27 Zhu Z F, Wang M & Li W, *Fiber Polym*, 16(2015) 1890.
28 Zhu Z F, Zhou Y Y & Zhang W G, *J China Text Univ (Eng Ed)*, 11(1994) 22.
29 Waters D L E, Henry R J, Reinke R F & Fitzgerald M A, *Plant Biotechnol J*, 4(2006) 115.
30 Doublier J L, Llamas G & Meur M L, *Carbohydr Polym*, 7(1987) 251.
31 Wong R B K & Lelievre J, *J Appl Polym Sci*, 27(1982) 1433.
32 Wurzburg O B, *Modified Starch: Properties and Uses* (CRC Press, Florida, USA), 1986, 3-16.
33 Wu S H, *Polymer Interface and Adhesion* (Marcel Dekker, New York, UAS), 1982, 359-448.
34 Hu G F, Chen J Y & Gao J P, *Carbohydr Polym*, 76(2009) 291.
35 Jansson A & Thuvander F, *Carbohydr Polym*, 56(2004) 499.
36 Sangseethong K, Lertphanich S & Sriroth K, *Starch-Stärke*, 61(2009) 92.
37 Ok H, Carr W W & Park H, *Text Res J*, 77(2007) 686.