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Effect of sulfosuccinylation of corn starch on the adhesion to viscose fibres at lower temperature

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Acid-thinned corn starch has been sulfosuccinylated to different levels of degree of substitution to study the adhesion of starch to viscose fibres at lower temperature. The sulfosuccinylated starches with a degree of substitution range 0.009 - 0.036 have been synthesized through a two-step reaction, namely starch maleation and sulfonation. The adhesion is evaluated in term of tensile force of slightly sized roving yarns. In addition, light transmittance, surface tension and retrogradation of cooked starch paste have also been measured for revealing the reason why the improvement on the adhesion is achieved. Sulfosuccinylated starch is characterized by FTIR and DSC. It is found that the sulfosuccinylation helps to overcome inherent drawback like insufficient adhesion of starch to fibres under lower temperature. The improvement is achieved through reducing the retrogradation and surface tension of cooked starch paste under lower temperature. It is recommended that the sulfosuccinylated starch is capable of being used at the temperature of about 65 °C, without significantly exhibiting the adverse influence on the adhesion when sulfosuccinylated starch has the degree of substitution value of 0.02-0.036.

Keywords: Sizing temperature, Corn starch, Sulfosuccinylation, Viscose fibres

1 Introduction

Starch, as a natural polysaccharide mainly from plant fruits and roots, is made up of D-glucosidic through bonds[1, 2]. It exhibits valuable behaviors such as easy biodegradation[3], low price[4], and abundant resource, having been widely used in the food, textile, and paper-making industries[5]. Starch as a size base material of warp sizing in textile industry, has been used for hundreds of years. However, natural starch is prone to retrogradation because of the association of starch hydroxyls between amylose chains under lower temperature[6]. Therefore, starch can’t meet with sizing demands of heat-sensitive fibres like viscose fibres. The reason is that the strength of viscose warp yarns will be greatly reduced if they are subjected to high temperature like sizing operation. Sized warp property, loom efficiency, and fabric quality will be adversely affected by the heated operation. In addition, warp sizing is an energy-consumed process, during which the cost of energy consumption to the total one input in warp sizing is about 15%. Currently, energy consumption in warp sizing is mainly caused by the higher sizing temperature. Therefore, there is an urgent need to develop the starch size that can be applied to size viscose warps under lower temperature, and it will greatly save energy in warp sizing.

Having sufficient adhesion to fibres is one of the valuable behaviors and essential demands for any sizing agents[7, 8]. The main function of the adhesion includes two aspects, namely (i) to adhere to the fibres together in warp yarn for increasing the yarn tensile strength, and (ii) to glue the hairs back onto the body of warp yarns by forming a film on the surface of yarns. Therefore, as one of the most important properties of sizing agents, the adhesion is closely related to the quality of sized yarns[9, 10]. It affects the physical and mechanical properties and determines the needs of size add-on[11]. For this reason, the adhesion has been received more and more attention recently. A great deal of research work has been done[12, 13].

Sulfosuccinylated starch (SSS) can be achieved by a two-step reaction, that is, through the maleation of maleic anhydride with acid-thinned starch (ATS) as shown in Scheme 1, and then the sulfonation of sodium hydrogen sulfite (Scheme 2) with the double bonds of maleic groups on maleated starch (MS) prepared in first step[14]. However, little is known about the influence of sulfosuccinylation on the adhesion of starch to viscose fibres. Currently, no investigation

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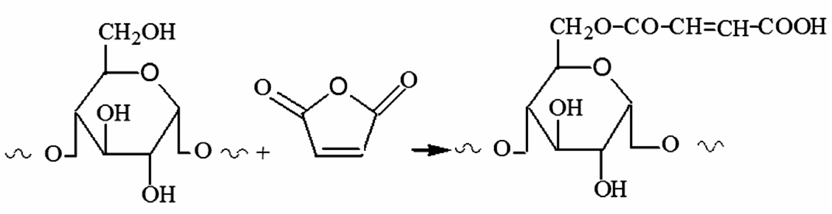
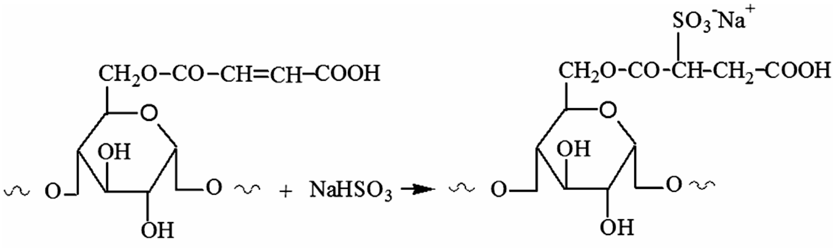


Scheme 1—Maleation of starch with maleic anhydride



Scheme 2—Sulfonation of MS with sodium hydrogen sulfite

has been reported on the use of sulfosuccinylation to improve the adhesion of starch under lower temperature. Accordingly, this study is especially undertaken to reveal if the sulfosuccinylation is able to overcome the shortcoming of starch for increasing the adhesion of starch to viscose fibres by evaluating the effect of degree of substitution (DS) and paste temperature on the adhesion of starch to the viscose fibres. It is speculated that the decrease in adhesion of starch under lower temperature is mainly due to retrogradation of paste, being resulted in by the aggregation of amylose chains through the re-association of hydroxyls between starch molecules[15]. Therefore, the retrogradation is particularly assessed by light transmittance and DSC. In addition, surface tension of a cooked starch paste shows substantial effect on wetting and spreading of paste onto the surface of fibres. Accordingly, the tension is measured during this study to reveal the reason why the sulfosuccinylation improves the adhesion of starch to viscose fibres.

2 Materials and Methods

2.1 Materials

Commercial corn starch with an apparent viscosity of 53 mPa.s was measured with NDJ-79 rotary viscometer (Electrical Mechanical Plant of Tongji University, Shanghai, China) using 6 % (w/w) concentration and 2028 s^{-1} shear rate at 95 °C.

Maleic anhydride, acetone, anhydrous sodium carbonate, hydrochloric acid, anhydrous sodium sulfate, anhydrous ethanol and sodium hydrogen sulfite, all of analytical reagent grades, were used directly as procured from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Pure viscose roving (590 tex, 52 twist factor, 38 mm fibre length and 1.33 dtex fineness) was used as substrate in the adhesion measurement.

2.2 Modification of Starch

The sulfosuccinylation of starch was implemented by a two-step method, namely maleation and sulfonation.

Prior to use, natural corn starch was defatted, refined, and acid-thinned with hydrochloric acid to reduce its excessive apparent viscosity as reported earlier[16, 17]. After these pretreatments, apparent viscosity of acid-thinned starch (ATS) was found to be 3 mPa.s.

2.2.1 Maleation of Starch

Maleation of ATS was carried out by dispersing 180 g ATS (dry weight), 3 g Na_2CO_3 and 18 g Na_2SO_4 with 540 mL of distilled water. The dispersion was heated to 30 °C under mechanical stirring. Maleic anhydride solution (30 % by mass) prepared with acetone was added into the dispersion slowly during 1.5 h. Meanwhile, the *p*H was maintained at 8-9 with 6 % (by wt) of Na_2CO_3 aqueous solution. After the maleic anhydride solution was dropped out, continuous stirring was done for 30min. Then, the product was neutralized to *p*H 6-7 with 2 mol/L HCl solution, filtered, washed three times with 75 % ethanol-distilled water solution, dried at 50 °C, pulverized, and sieved with 100-mesh sieve. The amounts of maleic anhydride were 5, 11, 16, and 31 g for the MS samples with the DS values of 0.01, 0.022, 0.028 and 0.04 respectively.

2.2.2 Sulfonation of MS

Sulfonation of MS was performed with sodium hydrogen sulfite. Sodium hydrogen sulfite was first dissolved in 334 mL of distilled water and then mixed with 180 g of MS (dry weight). The reaction was carried out under mechanical stirring at 40 °C for 5 h. Then, the product was neutralized to *p*H 6-7 with 6 % Na_2CO_3 solution, filtered, washed three times with ethanol-distilled water, dried at 40 °C, pulverized, and sieved with 100-mesh sieve. The SSS samples with the DS of 0.009, 0.020, 0.025 and 0.036 were prepared by using 6, 12, 15 and 21 g of sodium hydrogen sulfite respectively.

2.2.3 Characterization of Starch

Determination on DS values of maleic groups was based on titration of the double bonds. The double bonds of maleic groups react with Br_2, and then the residual Br_2 reacts with iodine. The excessive iodine was titrated with $Na_2S_2O_3$[18]. The DS_A denotes the DS value of maleic groups introduced on the starch chains, it was calculated as shown below:

$$x = \frac{(V_1 - V_2) \times C \times 0.0799}{W} \times 100 \qquad \ldots (1)$$

$$DS_A = \frac{162x}{79.904 \times (2 - 1.2265x)} \qquad \ldots (2)$$

where x (%) is the bromine value; V_1 (mL) and V_2 (mL), the volumes of the standard $Na_2S_2O_3$ solution consumed in blank and sample titration; C (mol/L), the concentration of the standard $Na_2S_2O_3$ solution; and W (g), the mass of the starch sample (dry weight); and 0.0799, the equivalent grams of bromine with 1mL of 1.000 mol/L standard $Na_2S_2O_3$ solution.

The DS_B indicates the DS value of sulfosuccinic groups on starch chains. Sulfonation efficiency and DS_B of the SSS were calculated using the following equations:

$$E = \frac{x_1 - x_0}{x_1} \times 100 \qquad \ldots (3)$$

$$DS_B = DS_A \times \frac{E}{100} \qquad \ldots (4)$$

where x_0 (%) and x_1 (%) are the bromine values of the SSS and MS respectively; and E (%), the sulfonation efficiency of the SSS.

2.3 Measurement on Paste Viscosity

Apparent viscosity of the starch samples was determined using NDJ-79 rotary viscometer with the method as reported earlier[19]. Starch was dispersed with distilled water to form concentration of 6 % (w/w) paste and gelatinized by heating the dispersion to 95 °C and maintaining it at this temperature for 1 h under mechanical stirring. Then, apparent viscosity of cooked starch paste was measured at 95, 80, 65, 50, 35 and 25 °C, and then the viscosity was recorded after every 30min over a period from 1h to 3 h after starch was gelatinized for calculating viscosity stability of cooked starch paste using the following equation:

$$\text{Viscosity stability} = (1 - \frac{v_{\max} - v_{\min}}{v}) \times 100 \qquad \ldots (5)$$

where $v_{\max}$ and $v_{\min}$ are the maximum and minimum of viscosity of cooked starch paste recorded over the period respectively; and v, the apparent viscosity of paste.

2.4 Measurement on Light Transmittance

Light transmittance of cooked starch paste was measured with Garg's method[20]. Four gram of starch sample (dry weight) was dispersed in 396 mL of distilled water to form a concentration of 1.0 % dispersion. The dispersion was heated to 95 °C and maintained at this temperature for 1 h under mechanical stirring. The cooked starch paste was cooled to 95, 80, 65, 50, 35 and 25 °C, and kept at the temperatures for 3 h. Then, light transmittance of the paste was determined on UV9600 spectrophotometer (Ruili Analytical Instrument Co., Ltd., Beijing, China) at 620 nm against distilled water blank.

2.5 Measurement on Adhesion

A roving method was used to assess the adhesion of sizing agents onto fibres. This method now in China has become a standard of evaluating the adhesion (FZ/T15001-2008, a criterion standard by Textile Association of China). Nine grams of dry starch and 891 mL of distilled water were added into a 1000 mL of flask, heated to 95 °C, and maintained at this temperature for 1h under mechanical stirring. Then, the paste was transferred to metal container immersed in water baths of 95, 80, 65, 50, 35 and 25 °C respectively. After keeping the paste in metal container for 3 h, the roving, being carefully wound onto flames, was impregnated with this paste for 5 min. Then, the roving was hung up, dried in air, and collected. The roving was placed at 20 °C and 65 % RH for 24 h before being measured. Finally, tensile force of the roving was measured with HD026 Electronic Strength Tester (Hongda Experimental Instruments Co., Ltd., Nantong, China).

2.6 FTIR Analysis

FTIR was used to verify the existence of maleic and sulfosuccinic groups on the starch chains. FTIR spectra were taken on Nicolet Nexus 470 FTIR spectrophotometer (Thermo Electron Corporation, USA) using KBr pellets between 4000 cm^{-1} and 500 cm^{-1} with a spectral resolution of 4 cm^{-1} for 32 scans.

2.7 Measurement on Surface Tension

One gram of starch (dry weight) was dispersed in distilled water to form 1, 2 and 3 % (w/w) dispersion, which was heated to 95 °C, maintained at the temperature for 1 h, and then the cooked starch paste was cooled to room temperature. The surface tension of cooked starch paste was then measured using the platinum plate method on A201 automatic surface tension instrument (Kino Industry Co., Ltd., USA).

2.8 DSC Measurement

Gelatinization enthalpies (ΔH_1) and retrogradation enthalpies (ΔH_2) were obtained using DSC Q200 (Ta Instruments-Waters LLC, USA) according to Gudmundsson's method[21]. Five grams of the starch samples (dry weight) were dispersed in distilled water to form 60 % (w/w) aqueous suspensions. Then, 5-10 mg of the starch suspension samples were transferred into the liquid crucibles. The samples were heated from 20 °C to 100 °C at a heating rate of 10 °C/min; meanwhile a sealed empty liquid crucible was used as a reference. The ΔH_1 was evaluated based on the area of the main endothermic peak and shown in terms of J/g of dry starch using the equipment software. Retrogradation of the starch suspension was also examined. In the retrogradation studies, the samples were heated in a baking oven at 105 °C for 30 min, and then stored at 20 °C for 6 h before DSC measurements were conducted. Then, the samples were measured at the temperature range of 20 - 140 °C and at a heating rate of 10 °C/min to evaluate the ΔH_2; meanwhile an empty liquid crucible was also taken as a reference.

3 Results and Discussion

3.1 Evidence of Sulfosuccinylation

Fourier transform infrared spectra of ATS, MS and SSS are illustrated in Fig. 1. Besides characteristic absorption peaks of ATS, two new adsorption peaks appeared in the spectrum of MS at 1721.16 cm^{-1} and 1577.80 cm^{-1} are corresponding to stretching vibration of the carbonyl and double groups respectively. The two new peaks demonstrate the maleic groups introduced on the starch backbones. One new absorption peak appeared in the spectrum of SSS at 1730.30 cm^{-1} is assigned to the stretching vibration of carbonyl groups. The other peak, appeared in the spectrum of SSS at 1209.80 cm^{-1}, corresponds to the stretching vibration of sulfonic groups. The two new peaks demonstrate the existence of sulfosuccinic groups introduced onto the starch backbones.

3.2 Characterization of SSS

Characterization of SSS is shown in Table 1. It is observed that as the amount (by mass) of maleic anhydride increases, reaction efficiency of maleation gradually reduces and DS_A increases. The reduction in reaction efficiency of maleation is mainly due to the decrease in active sites on starch chains. Reaction efficiency of sulfonation shows that over 90% double bonds have been sulfonated by sodium hydrogen sulfite.

3.3 Effect on Starch Paste

Influences of DS_B and temperature on apparent viscosity and viscosity stability of cooked starch paste are shown in Fig. 2 and Table 2 respectively. It can be observed from Fig. 2 that the viscosity increases with the rise in DS_B. Sulfosuccinylation of starch introduces sulfosuccinic groups onto starch chains.

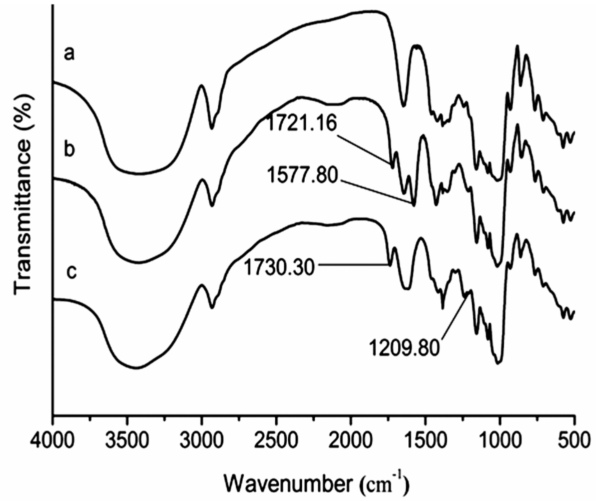


Fig. 1—FTIR spectra of (a) ATS, (b) MS, and (c) SSS

Table 1—Characterization of SSS

Maleation of ATS			Sulfonation of MS	
Maleic anhydride used, g	Maleation efficiency, %	DS_A	Sulfonation efficiency, %	DS_B
5	21.8	0.010	90.4	0.009
12	20.0	0.022	91.2	0.020
16	19.1	0.028	90.0	0.025
31	14.1	0.040	90.5	0.036

The groups are hydrophilic and enable to increase the hydrophilicity of starch chains, thereby enhancing intermolecular forces between starch and water. Therefore, the apparent viscosity of cooked SSS paste increases. In addition, sulfosuccinic groups are negatively charged and show repulsion between starch molecules in aqueous solution. The repulsion extends the macromolecular coils of starch in cooked starch paste. With the increase in amount of the groups, strong intermolecular forces and great extension can be expected. Therefore, the viscosity gradually increases as the DS_B increases. As the temperature decreases, the activity of starch chains decreases and intermolecular forces between starch molecules increases. As a result, association of hydroxyls among starch molecules tends to increase. The increment in the forces and association leads to a substantial increase in the viscosity.

As seen in Table 2, sulfosuccinylation of starch improves viscosity stability of cooked starch paste, particularly at 25-65 °C compared with the ATS. Under high temperature, lower stability of ATS paste is due to partial hydrolysis of glucosidic bonds of starch chains. And under lower temperature, higher stability of SSS paste may be attributed to the sulfosuccinic groups introduced onto starch chains. The groups weaken the formation of hydrogen bonds among starch hydroxyls through steric hindrance, and enhance the intermolecular forces between starch and water. Therefore, the reduction in viscosity of starch paste decreases and the stability increases.

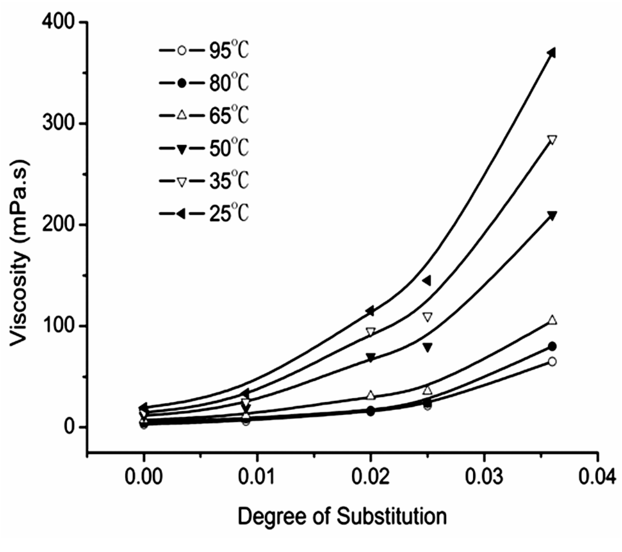


Fig. 2—Apparent viscosity of SSS at different temperatures

Table 2—Viscosity stability (%) of SSS at different temperatures

Starch	DS_B	95 °C	80 °C	65 °C	50 °C	35 °C	25 °C
ATS	0	86.0	83.3	76.0	65.2	58.6	55. 7
SSS	0.009	87.1	90.7	98.3	97.4	96.0	98.5
	0.020	89.6	95.1	98.4	97.2	94.7	95.7
	0.025	88.4	93.8	98.6	97.5	95.5	96.6
	0.036	92.3	93.8	95.2	95.2	96.5	97.3

3.4 Effect on Adhesion

The starches used in warp sizing as temporary adhesives are mainly to enhance the force of sized yarns by adhering fibres together, so as to withstand repeated drawing and impacting acted onto sized yarns during weaving operation[22]. Therefore, the influence of SSS on the adhesion to fibres must be evaluated. Generally, tensile force predicts the bonding force of sizing agents to fibres. The greater the tensile force, the stronger is the adhesion[8]. Table 3 shows the influences of starch sulfosuccinylation and paste temperature on the adhesion to viscose fibres. Compared to ATS, the tensile force of sized viscose roving has a lower reduction with the decrease in temperature after the sulfosuccinylation. The sulfosuccinylation plays an important role in improving the adhesion. As the DS_B rises, the adhesion to fibres increases gradually. The observation suggests that the sulfosuccinylation enables to strengthen the adhesion to viscose fibres under lower temperature compared with ATS. The adhesion of SSS to viscose fibres only shows a reduced decrement compared to that of ATS when the paste temperature is 65 °C or below. Therefore, the SSS is expected to be used in sizing viscose warps under lower temperature, and it will greatly save energy.

The increased adhesion induced by the sulfosuccinylation level of starch is due to the introduced sulfosuccinic groups. The groups increase the water dispersibility of starch. The higher the light transmittance, the greater is the water dispersibility. Therefore, the water dispersibility of starch was illustrated through light transmittance as shown in Fig. 3. It can be found that sulfosuccinylation can significantly enhance water dispersibility of starch compared with that of ATS and water dispersibility gradually increases as the DS_B increases. It has been expounded that worse water dispersibility produces incomplete wetting and spreading of starch paste onto the surface of fibres which results in interfacial defects and stress concentration around unwetted or outspreaded fields[23]. So, the sulfosuccinylation weakens the occurrence of incomplete wetting and

Table 3—Effects of sulfosuccinylation level and paste temperature on the adhesion to viscose fibres

DS_B	95°C		80°C		65°C		50°C		35°C		25°C	
	S_m	CV	S_m	CV	S_m	CV	S_m	CV	S_m	CV	S_m	CV
	N	%	N	%	N	%	N	%	N	%	N	%
0	86.9	4.75	85.2	4.65	83.6	4.44	81.4	6.25	79.1	6.56	76.2	6.83
0.009	98.3	3.97	97.2	3.46	96.9	2.41	96.1	2.96	96.0	2.87	95.7	3.22
0.020	100.2	2.98	99.3	2.87	98.5	2.67	97.2	3.25	96.9	3.46	96.4	3.85
0.025	100.7	2.86	100.1	2.85	99.3	2.70	98.8	3.36	98.5	3.40	97.8	3.45
0.036	101.0	2.77	100.7	2.75	100.5	2.76	99.8	2.83	99.3	3.15	98.9	3.19

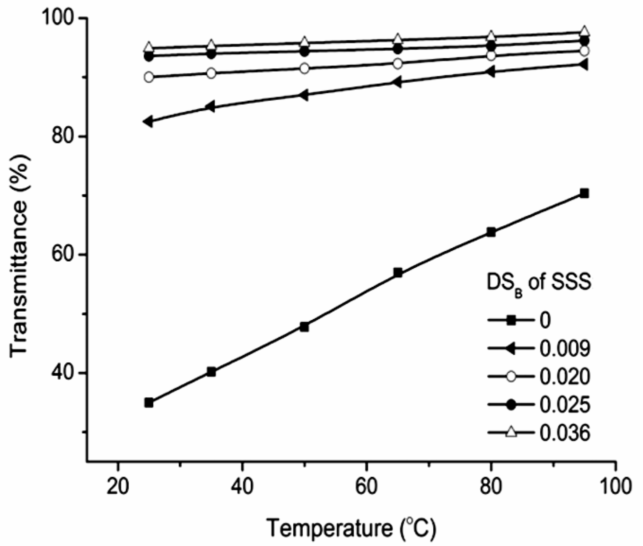


Fig. 3—Light transmittance of cooked starch paste at different temperatures

spreading of cooked starch paste onto the surface of fibres, and improves the wetting and spreading as the sulfosuccinylation level increases. It has been described that incomplete wetting and spreading are detrimental to the adhesion[24]. Thus, the sulfosuccinylation enables the improvement in adhesion to viscose fibres, and the adhesion increases with the increase in sulfosuccinylation level.

In addition, amphiphilic structure of SSS through the groups introduced on starch chains decreases the surface tension of paste as shown in Fig. 4. It has been shown that high surface tension usually results in poor wetting and spreading of cooked starch paste onto the surface of fibres[25]. So, the surface tension exhibits significant impacts on the adhesion of starch to fibres. Therefore, the surface tensions of gelatinized starch pastes under different levels of DS_B should be assessed. The influences of the DS_B on the surface tensions of pastes are presented in Fig. 4. It can be observed that the surface tensions of pastes decrease gradually with the increases in DS_B.

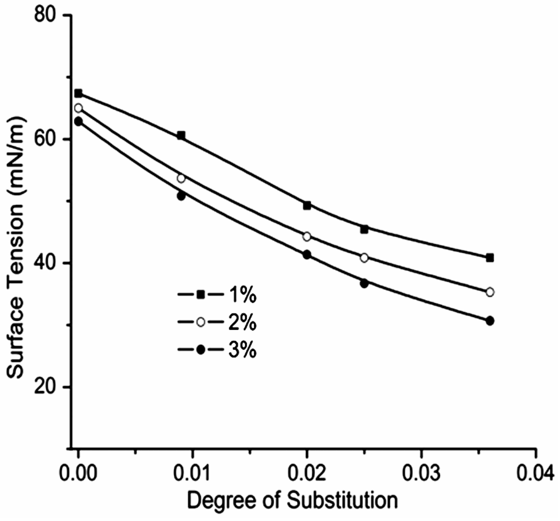


Fig. 4—Surface tensions of 1, 2 and 3% starch pastes under different levels of degree of substitution (DS_B)

The sulfosuccinylation has the ability to reduce surface tension of cooked starch paste because of its surfactant characteristic. The characteristic is that surfactant has hydrophobic and hydrophilic group simultaneously[26]. The hydrophilic part of surfactant is prone to be soluble in water, whereas the hydrophobic part tends to depart from water when the concentration of solution is much lower. These make the aggregation of surfactant on the surface of solution, and obviously reduce the surface tension of solution. In the SSS molecules, the hydrocarbon ring can be seen as the hydrophobic part[27], whereas the hydrophilic part is the hydroxyl group and sulfosuccinic group. Therefore, sulfosuccinylation can decrease the surface tension of cooked starch paste because of surfactant characteristic of the SSS. The higher the DS_B, the more is the aggregation of the SSS molecules on the surface of solution. Thus, the surface tension of paste continuously decreases with the increase in DS_B.

During the adhesion of starch paste to fibres, it demands complete wetting and spreading. Wetting is a process in which liquid replaces the air on the surface of solid; meanwhile, the surface of solid is occupied by the solid-liquid interface. Spreading is a process in which liquid extends on the surface of solid by solid-liquid interface instead of solid-gas interface. In the two processes, according to the principle of energy change, if the increase of liquid energy is lower than the decrease in solid energy, it will take the occurrence of automatic wetting and spreading. In addition, the value of liquid surface tension may indicate the increase in liquid energy. So it indicates that surface tension of the cooked SSS paste decreases gradually with the addition of DS_B; this is helpful to wetting and spreading of starch paste onto the surface of viscose fibres. Wetting and spreading become better and better with the gradual decrease in surface tension. Better wetting and spreading improve the adhesion. Therefore, it can be inferred that adhesion gradually increases with the gradual addition of DS_B. This is in agreement with the data presented in Table 3.

Furthermore, the groups reduce the retrogradation of starch evaluated by DSC. Retrogradation of starch has been described as a process of gelatinized starch paste from an amorphous state to a more orderly state[28]. It is meaningful to understand that retrogradation can be considered as a two-step process, an initial short-term step is related to amylose crystallization, and a long-term step involves amylopectin crystallization[29, 30]. The DS dependence of ΔH_1 and ΔH_2 of SSS is presented in Table 4. It can be found that ΔH_1 and ΔH_2 of SSS decrease as compared to ATS. In the gelatinization process, ΔH_1 is mainly due to the heat absorption during the fracture of hydrogen bond between starch molecules. The sulfosuccinic groups introduced on starch chains decrease the association of hydroxyls between starch molecules through steric hindrance. Therefore, the ΔH_1 of SSS is lower than that of ATS. The decrease in ΔH_2 of SSS as compared to the ATS is mainly due to the results of starch retrogradation in re-association of starch molecules, but it is in less ordered form, and hence produces less stable form than those in the natural starch granules[31]. In addition, the higher the DS_B, the stronger is the reduction of sulfosuccinic groups to the retrogradation due to re-association of hydrogen bond between starch molecules. So, the ΔH_2 of the SSS gradually decreases with the increase in DS_B. Hence, sulfosuccinylation of starch reduces the retrogradation, and the reduction in the retrogradation increases with the rise in sulfosuccinylation level, thereby improving the wetting and spreading of paste onto the surface of viscose fibres. Therefore, the SSS is capable of playing an important role in the adhesion as the sulfosuccinylation level increases.

Table 4—Effect of sulfosuccinylation on the ΔH_1 and ΔH_2 of starch

DS_B	ΔH_1, J/g	ΔH_2, J/g
0	6.548	1.486
0.009	5.629	0.456
0.020	3.807	0.218
0.025	3.327	0.183
0.036	2.947	0.160

Besides, the groups interfere with the formation of hydrogen bonds among starch hydroxyls through steric hindrance, thereby reducing the internal stresses of adhesive layers and enhancing their toughness. It has been clarified that internal stresses of adhesive layers are detrimental to an adhesion[32], and toughening adhesive layers are considerably important to decrease the stresses[33]. When the layers include brittle materials like starch, the stresses are generally strong, which is harmful to the adhesion. Apparently, the introduced sulfosuccinic groups supply plasticization for starch layers, and with the increase in sulfosuccinylation level of starch, the plasticization increases through the rise in steric hindrance of sulfosuccinic groups. Therefore, the adhesion of starch to viscose fibres gradually increases with the increase in sulfosuccinylation level of starch.

The less reduction in adhesion with the decrease in temperature after the sulfosuccinylation is due to the increase in water dispersability of starch under lower temperature. The decrease in starch retrogradation particularly assessed by light transmittance is shown in Fig. 3. It is clearly observed from the figure that ATS paste has an obvious drop in light transmittance as the paste temperature reduces, whereas the light transmittance of SSS paste is resistant to the range of temperature. The observation means that the sulfosuccinylation enables to reduce the retrogradation of starch paste and thus enhances the dispersibility of starch in aqueous paste under lower temperature. Moreover, increasing sulfosuccinylation level continuously enhances the decrease in retrogradation and the dispersibility under lower temperature.

It is well known that starch is principally composed of linear amylose and branched amylopectin[34], and with the decrease in temperature, natural starch paste shows retrogradation. The retrogradation of gelatinized starch paste is due to the association of hydroxyls between linear amylose chains, which shows that the linear amylose and straight part of branched amylopectin are in parallel arrangement, forming macromolecular aggregates[35]. The aggregates stop the light transmittance, and make the light transmittance to decrease as the temperature decreases. Therefore, the water dispersibility reduces and retrogradation rises with the decrease in temperature. However, the hydrophilic sulfosuccinic groups introduced onto the starch backbones through the sulfosuccinylation disturbs the regular arrangement of amylose and interferes with the association of hydroxyls due to their steric hindrance. Therefore, sulfosuccinylation enhances the water dispersibility of starch and reduces the retrogradation of cooked starch paste under lower temperature.

4 Conclusion

It can be concluded, based on the pervious experimental results and discussion, that the sulfosuccinylation of starch is an effective way for improving the adhesion to viscose fibres. The tensile force of SSS onto viscose fibres obviously enhances as compared to ATS, even if the sulfosuccinylation is at very low extent. The sulfosuccinylation introduces hydrophilic sulfosuccinic groups onto starch chains, thereby markedly increasing light transmittance, indicating the increased water dispersibility and reduced retrogradation. The increased water dispersibility and reduced retrogradation cause the tensile force to increase. In addition, the groups interfere with the formation of hydrogen bonds among starch hydroxyls through steric hindrance, thereby reducing the internal stresses of adhesive layers and reducing their brittleness. Besides, amphiphilic structure of SSS deceases the surface tension of cooked starch paste. Accordingly, the sulfosuccinylation produces an important effect on the adhesion, and the adhesion evidently enhances as the sulfosuccinylation extent increases. The sulfosuccinylation of starch also improves the adhesion to viscose fibres under lower temperature. And the tensile force has a lower reduction as the temperature decreases as compared to ATS, which is mainly due to the decrease in starch retrogradation through the increased water dispersibility of starch and steric hindrance of sulfosuccinic groups. Therefore, the sulfosuccinylation is capable of strengthening the adhesion to viscose fibres under lower temperature, and the SSS supplies a lower reduction in the adhesion as compared to ATS. Thus, sulfosuccinylation is able to overcome insufficient adhesion of starch to fibres under lower temperature and enables to be applied at the temperature of about 65 °C without significantly exhibiting the adverse influence on the adhesion when SSS has a DS value of 0.02-0.036.

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