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Carbohydrate Polymers 69 (2007) 123–129

Carbohydrate Polymers

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Synthesis of cationic hydrolyzed starch with high DS by dry process and use in salt-free dyeing

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Received 19 August 2006; received in revised form 12 September 2006; accepted 18 September 2006
Available online 15 November 2006

Abstract

Cationic hydrolyzed starch was prepared by hydrolyzed maize starch with 2,3-epoxypropyltrimethyl ammonium chloride by dry process. Experiments showed that 80 °C, 1 h, 0.1:1 of molar ratio of sodium hydroxide to cationizing reagent were suitable for cationization, and high degree of substitution of cationic hydrolyzed starch was obtained. The structures of the hydrolyzed maize starch and cationic hydrolyzed starch were characterized by IR spectroscopy, scanning electronic microscopy and X-ray diffraction. The synthesized cationic hydrolyzed starch was employed in salt-free dyeing of reactive dyes. It showed that high dye fixation and level dyeing were obtained by pretreating cotton with the cationic hydrolyzed starch with low viscosity and high DS. Besides, wash fastness and rub fastness were not affected. The highest dye fixation in salt-free dyeing is higher than that of conventional dyeing by 20.3%, 0.9% and 18.4% for C.I. Reactive Red 2, C.I. Reactive Blue 19 and C.I. Reactive Yellow 145, respectively.

Keywords: Cationic hydrolyzed starch; Salt-free dyeing; Low viscosity; High DS

1. Introduction

Cationic starches are important commercial modified starches, and widely used as additives in the paper, textile, oilfield drilling, wastewater treatment or cosmetic industry because of their relatively low price, excellent properties and biodegradability (Heinze, Haack, & Rensing, 2004; Khalil & Aly, 2001; Zhang, 2001). Most commercial cationic starches have low DS less than 0.2 (Heinze et al., 2004), but cationic starches with high DS possess preferable properties and potential applications. Cationic starches are usually produced by etherifying reaction of starch with the tertiary amino and quaternary ammonium cationizing reagents, especially quaternary ammonium cationizing reagents, such as 3-chloro-2-hydroxypropyltrimethylammonium chloride (QUAB188) or 2,3-epoxypropyltrimethylammonium chloride (QUAB151) (Kaki et al., 2003). Among various processes, dry process containing commonly 10 to 40 weight percent of water (Stober, Reinhard et al., 1988; Roerden et al., 1993; Likitalo et al., 2005) is proposed and applied due to high degree of substitution (DS), high reaction efficiency, free-pollution, without gelatinization inhibitors, etc. (Heinze et al., 2004; Khalil, Farag, Dokki, & Cairo, 1998; Ju, Zhang, & Yang, 2000).

In general, large quantities of salt (30–150 g/L) are needed to overcome the static repulsion between cotton fibers and reactive dyes in order to promote dyeability, but simultaneously result in heavy environmental pollution, so research on salt-free dyeing is an active area (Hall et al., 1996; Chattopadhyay, 2001; Virkler et al., 2002; Ma, Zhang, & Tang, 2005). Our previous study showed that cotton pretreated with cationic starch exhibited improved dye fixation by continuous dyeing in the absence of salt (Zhang, Ma, & Ju, 2005), but failed to apply in exhaust dyeing method. Without leveling agent, level dyeing was difficult to obtain due to high viscosity of cationic maize

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doi:10.1016/j.carbpol.2006.09.011

starch. However cationic hydrolyzed starch has low viscosity, which may benefit dye exhaustion and obtain uniform dyeing easily. No previous attempt appears to have been made to study the application of cationic starches with low viscosity in salt-free dyeing by exhaust dyeing method.

The aim of this work was to synthesize cationic starches with low viscosity and high DS by dry process so as to realize uniform dyeing and high dye fixation in salt-free dyeing. In this paper, synthesis conditions of dry process for the achievable DS were investigated. The obtained cationic hydrolyzed starch was characterized by means of IR, scanning electronic microscopy (SEM) and X-ray diffraction. Viscosity and the weight-average molar mass (M_w) of cationic hydrolyzed starch were determined. The effects of cationic hydrolyzed starches on fixation and fastness properties of reactive dyes in exhaust dyeing were studied.

2. Materials and methods

2.1. Materials

The starch material used was maize starch of food-grade quality. The starches were dried at 100 °C before use. Sodium hydroxide and epichlorohydrin were of analytical grade. Trimethylamine aqueous solution and hydrochloric acid were used. QUAB151was laboratory prepared by trimethylamine and epichlorohydrin (Childers & Roerden, 2000). Cotton (150 g/m^2), bleached, desized and mercerized, was purchased from Testfabrics, Inc., Shanghai. The reactive dyes (Table 1) were obtained from Shanghai Dyestuff Co. and used as received. Their structures were listed in Fig. 1.

Four types of hydrolyzed starches namely H_1-, H_2-, H_3- and H_4-starch were prepared by 0.1 N, 0.5 N, 1 N and 2 N HCl treatment of maize starch at 50 °C for 2 h using a liquor/starch ratio 5, respectively.

2.2. Methods

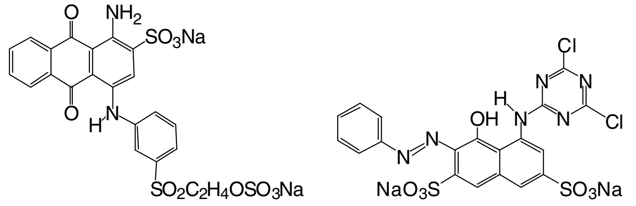
2.2.1. Synthesis of cationic hydrolyzed starch by dry process

A mixture (approximately 20% H_2O) of etherifying reagent and hydrolyzed starch pretreated with 1.5 N NaOH was stirred constantly for nearly 1 h at room temperature, then maintained for 0.5–3 h at certain temperature. The cationic starch was obtained by immersing the rough product in alcohol, the pH was adjusted to 7 using acetic acid. The product was then filtered and washed with alcohol and soxhlet extracted for 12 h using an ethanol: water mixture 80:20 (v/v) and finally dried at vacuo. The tests were repeated.

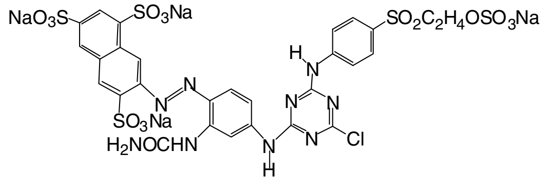
Table 1
The dyes used in the experiments

Commercial name	C.I. generic name	Amount of dye applied (% o.w.f)*
Reactive Brilliant Red X-3B	C.I. Reactive Red 2	2
Reactive Brilliant Blue KN-R	C.I. Reactive Blue 19	3
Reactive Brilliant Yellow M-3RE	C.I. Reactive Yellow 145	1

* o.w.f: of weight fiber.



C.I. Reactive Red 2 C.I. Reactive Blue 19



C.I. Reactive Yellow 145

Fig. 1. Molecule structures of the dyes used in the experiment.

2.2.2. Pretreatment of cotton and dyeing procedure

Pad-bake method was used for pretreatment of cationic starch on cotton. Twenty milliliters neutral solution of cationic starch was used as the pad-bath for 1 g cotton. The pressure on the mangle was adjusted to give 80% wet pick-up, and pad proceeded with 2 dips (3 min for one dip), 2 nips, then the samples were baked directly at 100 °C for 10 min in a Rapid baker. The treated fabrics were ready for dyeing.

Exhaust dyeing was carried out using a liquor ratio of 20:1. Dyeing of the pretreated cotton was commenced at 20 °C, and kept at this temperature for 30 min. Fixation temperature was chosen according to the recommended fixation temperature in the conventional dyeing. Fixation step proceeded 40 min and 10 g/L sodium carbonate was used for dye fixation. Conventional dyeing on the untreated cotton followed the procedures recommended by the dye manufacturer in the presence of anhydrous sodium sulphate (60 g/L), and 10 g/L sodium carbonate was also added for dye fixation. After dyeing, the cotton fabric was removed from the bath and rinsed thoroughly in cold, hot then cold water. The rinse was collected for measurement of dyebath exhaustion. Then the dyed fabric was subjected to boiling in a solution containing 2 g/L anionic detergent LS (Shanghai) for 15 min until no dye was removed off, and then rinsed. The rinse was collected for measurement of dyebath fixation and the fabric was allowed to air dry. The tests were repeated.

2.2.3. Measurements

DS of cationic starch was determined by the Kjeldahl method. DS and reaction efficiency (RE%) were calculated according to Eqs. (1) and (2):

$$\mathrm{DS} = 162.15 \times \mathrm{N\%}/(1401 - 151.64 \times \mathrm{N\%}) \quad (1)$$

$$\mathrm{RE\%} = \mathrm{DS}/(\mathrm{QUAB151/starch\ molar\ ratio}) \times 100\% \quad (2)$$

The dye exhaustion (E) was determined using HP 8453 UV–vis spectrophotometer by sampling the dyebath before and after the dyeing process as in Eq. (3). Dye fixation (F) was calculated by Eq. (4), wherein A_2 was measured using HP 8453 UV–vis spectrophotometer by comparing the absorbance of standard soap bath and that of the soap bath after soaping step. It should be specialized that all the absorbance were got under the same volume of the liquor.

$$E = (A_0 - A_1)/A_0 \times 100\% \quad (3)$$

$$F = E \times (A_0 - A_1 - A_2)/(A_0 - A_1) \times 100\% \quad (4)$$

where A_0 is the absorbance of the initial dyebath, A_1 is the absorbance of the dye dyebath after the dyeing process, and A_2 is the absorbance of the soap bath after soaping process.

Wash fastness was tested according to GB/T3921-97 using S-1002 two bath dyeing and testing apparatus (Roaches Co., UK). Rub fastness was tested according to GB/T3920-97 using Y(B)571-II crockmeter.

Viscosity of cationic hydrolyzed starches dissolved in water (2 wt.%) was measured at 15 °C by means of a rotational viscosimeter NDJ-1 (Shanghai China) at a suitable shear rate.

IR spectra were recorded on a FT/IR-430 Infra-Red Spectrometer (Thermo Electron Corporation, Japan) using KBr pellets. Information on granular characteristics of starch and derivatives was provided by scanning electronic microscopy with a JEM-1200EX Electron Microscope (JEOL). The X-ray diffraction which may show the degree of crystallinity of starch and its derivatives was measured stepwise in the 2θ between 4° and 60° by a Rigaku diffractometer *D*/max-2400 (Rigaku, Japan). Monochromatic (Graphite monochromator) Cu-Kα_1-radiation (40 kV, 100 mA) was used. The weight-average molar mass (M_w) of cationic hydrolyzed starch was determined by GPC with a WATERS-515 (Waters Corporation, USA).

3. Results and discussion

3.1. Synthesis of cationic hydrolyzed starches by dry process

Cationic hydrolyzed starch (2-hydroxypropyltrimethylammonium chloride hydrolyzed starch) (Fig. 2) is synthesized by hydrolyzed starch with QUAB151, and NaOH as catalyst. Cationization of the O-2-position shows a strong preference for the O-3- and O-6-position (Heinze et al., 2004; Tüting, Wegemann, & Mischnick, 2004).

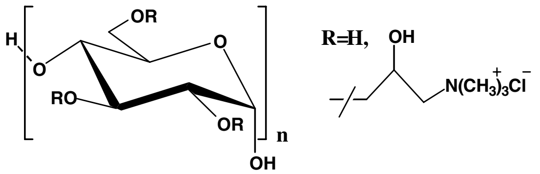


Fig. 2. Structure of cationic hydrolyzed starch.

3.1.1. Influence of reaction temperature and time on DS of cationic H_3-starch

A molar ratio of sodium hydroxide, QUAB151 to AGU of 0.1:0.6:1 was taken. It was evident from the data that the etherification reaction was unsuitable at much lower or higher temperature (Fig. 3). At lower temperature of 60 °C, swell of starch granules and diffusion of reagents were difficult, etherification reaction proceeded slowly. At higher temperature of 100 °C, reaction efficiency decreases with the decomposition and hydrolysis of cationization reagent, gelation of starch granules and vaporation of water. But swell of starch granules and diffusion of reagents improved with the increase of the temperature, so high DS of 0.48–0.49 and reaction efficiency of 80–82% could be obtained at 80 °C or 90 °C after only1-1.5 h. Because of hydrolysis of cationic starch and cationizing reagent, DS decreased while reaction time prolonged. Hence 80 °C and 1 h were the most desirable condition for the reaction. Yield of cationic hydrolyzed starches was more than 95%.

3.1.2. Influence of sodium hydroxide concentration on DS of cationic H_3-starch

Certain NaOH concentration in the etherification reaction system is necessary to activate the starch, but the hydrolysis of the cationization reagent and cationic starches resulted from addition of alkali should be controlled as low as possible. As expected, at low alkaline concentration, the reaction proceeds slowly and the reaction efficiency was low. With the increase of alkali concentration, the hydrolysis of the epoxide to form the diol and th‘e hydrolysis of cationic starch increased, thereafter DS of the product and the reaction efficiency gradually decreased. When molar ratio of base

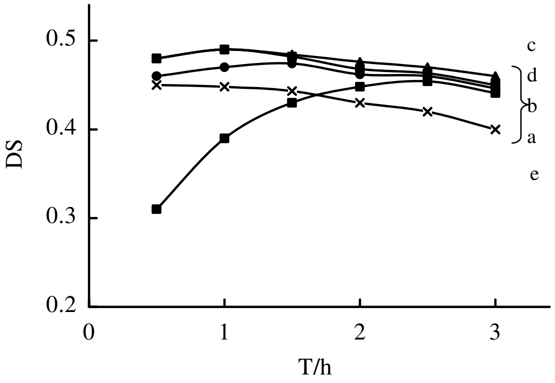


Fig. 3. Effect of reaction temperature and time on DS of cationic H_3-starch. (a) 60° ; (b) 70°; (c) 80°; (d) 90°; (e) 100°C.

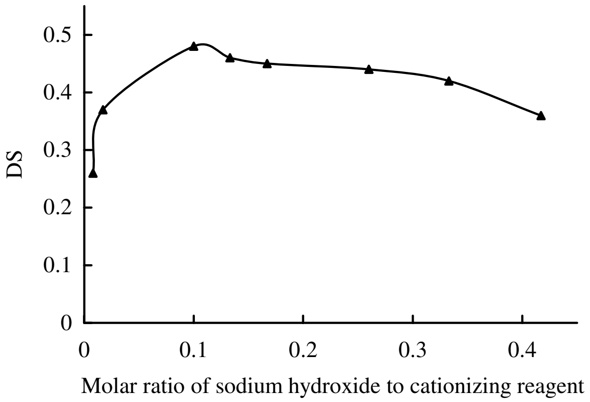


Fig. 4. Effect of sodium hydroxide concentration on DS of cationic H_3-starch.

to etherifying reagent was 0.1:1, DS of 0.48 and reaction efficiency of 80% were obtained (Fig. 4). So molar ratio of base to etherifying reagent of 0.1:1 was reasonable. In the experiment, yield was also more than 95%. Molar ratio of QUAB151 per AGU of 0.6:1 and H_3-starch were used, and reaction was completed at 80 °C after 1 h.

3.1.3. Preparation of cationic hydrolyzed starches with different viscosities

The reaction proceeded by using a molar ratio of sodium hydroxide, QUAB151 to AGU of 0.1:1:1, and maintained at 80 °C for 1 h. $H_{1\text{-}4}$ starches were used. Cationic $H_{1\text{-}4}$ starches with DS of 0.7 and reaction efficiency of 70% were then obtained. Yield of cationic $H_{1\text{-}4}$ starches was more than 95%, respectively. It is obvious that viscosity of cationic hydrolyzed starches decreased with the degree of degradation of maize starch, shown in Table 2. M_w of cationic H_3- and H_4-starch with lower viscosity is 2.17×10^5 g/mol and 2.00×10^5 g/mol, respectively. Comparing with M_w, viscosity is more easily determined.

3.2. Characteristics of H_3-starch and cationic H_3-starch

3.2.1. IR spectra of H_3-starch and cationic H_3-starch

IR spectra confirmed the existence of the cationic groups of cationic H_3-starch with a DS of 0.48 (Fig. 5). The spectrum of the cationic H_3-starch shows not only the characteristic starch backbone at 1154, 1082, 1018 and 570 cm^{-1}, but also the additional adsorption bands of the quaternary ammonium groups at 3021 cm^{-1} (CH, CH_3) and 1491 cm^{-1} (CN).

Table 2
Viscosity and M_w of cationic hydrolyzed starch

Cationic hydrolyzed starch	H_1-starch	H_2-starch	H_3-starch	H_4-starch
η (mPa s) (15 °C)	1200	180	7	6
M_w ($\times 10^5$ g/mol)	—	2.64	2.17	2.00

3.2.2. SEM photos of H_3-starch and cationic H_3-starch

Shapes of H_3-starch and cationic H_3-starch can be observed by scanning electronic microscopy (Fig. 6). Starch granules keep integrity after hydrolysis by acid with some holes existing on the surface. However cationic hydrolyzed starch showed severe damage after dry cationization process.

3.2.3. X-ray diffraction patterns of H_3-starch and cationic H_3-starch

X-ray diffraction showed that the amount of amorphism increased after cationization of hydrolyzed starch (Fig. 7). This meant that part of starch crystalline structure was destroyed by the dry cationizing reaction. Amorphism structure is looser than crystalline structure, this may be one of the reasons that DS of cationic starch by dry process is higher than that yielded by wet process. It was ever found part of the crystalline structure in relation to the native potato starch was destroyed during dry cationisation process whereas the remaining crystallites were not affected by wide-angle X-ray diffraction, but the crystalline structure did not change during wet cationization process (Radosta et al., 2004).

3.3. Application of cationic hydrolyzed starches in salt-free dyeing

3.3.1. Effect of DS of cationic hydrolyzed starch on dye fixation

In the experiments, cationic H_3-starch with different DS was used. Concentration of cationic starch was 15 g/L. Dye fixation increased along with the increase of DS of cationic H_3-starch (Fig. 8). Cationic starch with high DS has more positive charges to counteract static repulsion between fiber and reactive dyes, so more reactive dyes can adsorb on fibers during dyeing process. Consequently, the chance of formation of covalent bonds between reactive dyes and fibers increases and dye fixation is certainly enhanced. When DS increased from 0.37 to 0.70, dye fixation increased from 45.9%, 46.3% and 53.4% to 59.2%, 62.9%

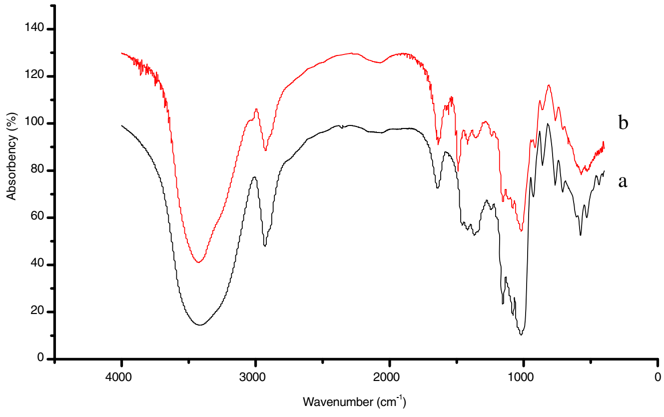


Fig. 5. IR spectra of H_3-starch (a) and cationic H_3-starch with a DS of 0.7 (b).

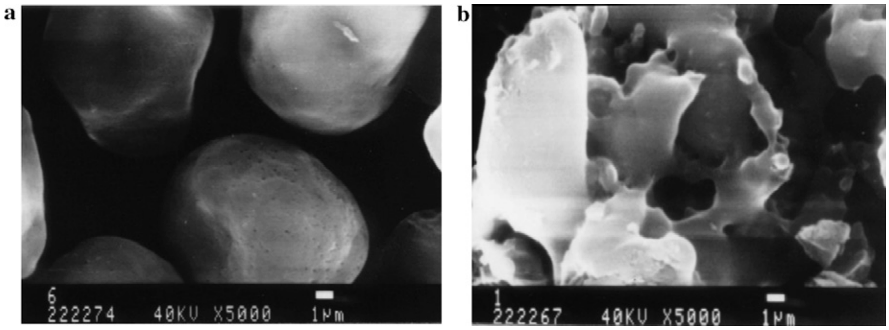


Fig. 6. SEM photos of H_3-starch (a) and cationic H_3-starch with a DS of 0.48 (b).

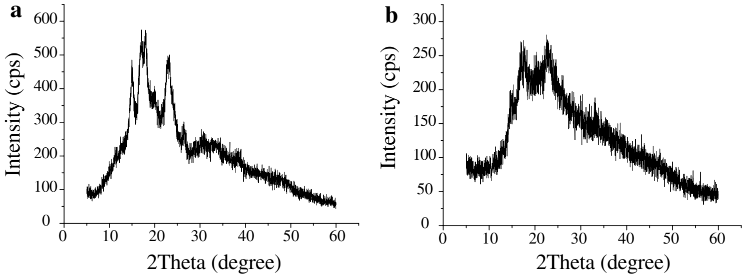


Fig. 7. X-ray diffraction patterns of H_3-starch (a) and cationic H_3-starch with a DS of 0.48 (b).

and 67.1% for C.I. Reactive Red 2, C.I. Reactive Blue 19 and C.I. Reactive Yellow 145, respectively. Dye fixation pretreated with the cationic H_3-starch had reached practical result from conventional dyeing with salt for the three reactive dyes.

3.3.2. Effect of concentration of cationic hydrolyzed starch on dye fixation

From Fig. 9, dye fixation was enhanced with the increase of concentration of cationic H_3-starch, but it was decreased after the concentration exceeded certain values. At lower concentration, the amount of cationic H_3-starch adsorbed on cotton fabrics was not enough to overcome the static repulsion between fiber and reactive dyes, so dye fixation was enhanced with the increase of concentration of cationic H_3-starch. At much higher concentration of cationic starch solution, some cationic starch pretreated on the surface of fiber was removed from the fiber during subsequent dyeing process, and flocculation of anionic dyes was resulted. Then neither level dyeing nor high dye fixation could be achieved. The highest dye fixation for C.I. Reactive Red 2, C.I. Reactive Blue 19 and C.I. Reactive Yellow 145 was, respectively, 69.4%, 73.8% and 75.3%, and the corresponding concentrations of cationic H_3-starch were, respectively, 30 g/L, 22.5 g/L and 17.5 g/L. Furthermore eco-friendly cationic starch solution used to pretreat cotton could be continuously used.

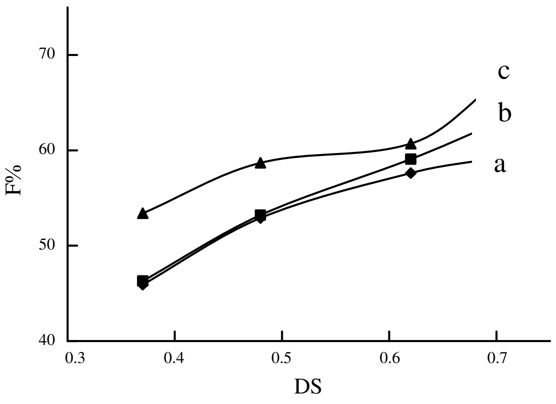


Fig. 8. Effect of different DS of cationic H_3-starch on dye fixation (a) C.I. Reactive Red 2; (b) C.I. Blue 19; (c) C.I. Reactive Yellow 145.

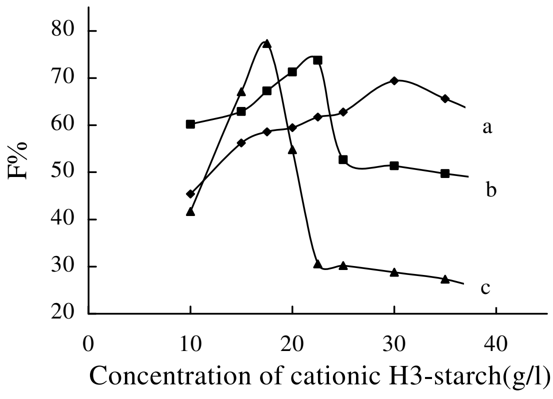


Fig. 9. Effect of concentration of cationic H_3-starch on dye fixation. (a) C.I. Reactive Red 2; (b) C.I. Reactive Blue 19; (c) C.I. Reactive Yellow 145.

Table 3
Effect of viscosity of cationic hydrolyzed starch on level dyeing and dye fixation

Cationic hydrolyzed starch	Dye fixation (%)			Level dyeing
	C.I. Reactive Red 2	C.I. Reactive Blue 19	C.I. Reactive Yellow 145	
Cationic H_1-starch	47.2	49.9	57.1	No
Cationic H_2-starch	52.1	55.2	60.7	No
Cationic H_3-starch	59.2	62.9	67.1	Yes
Cationic H_4-starch	60.6	64.2	69.9	Yes

Concentration of cationic hydrolyzed starch was 15 g/L.

Table 4
Comparison of fixation and fastness properties between salt-free dyeing and conventional dyeing

Dye	Process	F (%)	Wash fastness		Rub fastness	
			Change	Staining	Dry	Wet
C.I. reactive	1	69.4	4–5	4	3–4	3
Red 2	2	49.1	4	4	4	4
C.I. reactive	1	73.8	4–5	4–5	3–4	3
Blue 19	2	72.9	4–5	4	4	3–4
C.I. reactive	1	75.3	4–5	4–5	4	3
Yellow 145	2	56.9	4	4–5	4–5	4

1, salt-free dyeing; 2, conventional dyeing.

3.3.3. Effect of viscosity of cationic hydrolyzed starch on dyeing

Cationic hydrolyzed starches ($DS = 0.7$) with various viscosities were used. Cationic starch with lower viscosity led to higher dye fixation and more uniform dyeing by visual examination (Table 3). The reason for it is that low viscosity benefits diffusion and penetration of cationic starch to fibers uniformly, so reactive dyes can uniformly diffuse and penetrate to fibers by ion–ion interaction between the cationic starch and anionic dyes. Then the dyes are fixed easily on the fibers under alkaline condition, thus level dyeing and high dye fixation can be obtained. On the contrary, cationic starches with high viscosity only adhere to the surface of fibers and it is difficult for them to achieve uniform pretreatment. As a result, reactive dyes are difficult to diffuse and penetrate to fibers and only adsorbed on the surface of fibers unevenly. Furthermore, the reactive dyes cannot be strongly fixed on fibers, and partial dyes are removed off during alkaline fixation, so level dyeing and high dye fixation cannot be realized. Only by pretreatment with cationic hydrolyzed starch of low viscosity, such as cationic H_3- and H_4-starch, can both level dyeing and high dye fixation be obtained in salt-free dyeing.

3.3.4. Comparison of salt-free dyeing and conventional dyeing

Comparison of fixation, wash fastness and rub fastness of dyeings between salt-free dyeing and conventional dyeing was shown in Table 4. Optimal datum were selected based on the above investigation.The dye fixation showed that fixation increased for the dyes used on the cotton pretreated with cationic H_3-starch by exhaust dyeing. For C.I. Reactive Red 2, C.I. Reactive Blue 19 and C.I. Reactive Yellow 145, fixation increase of 20.3%, 0.9% and 18.4% was achieved, respectively. And the wash fastness was excellent and rub fastness was still good, which meant that pretreatment of cationic starch did not influence these two fastness properties of the dyes.

4. Conclusions

By studying the synthesis of cationic hydrolyzed starches by dry process, it was shown that dry process was beneficial for cationization of starch, and high DS can be obtained. SEM photos and X-ray diffraction patterns obviously showed that dry process damaged the starch granules, and the amount of amorphism increased during dry process. Salt-free dyeing of cotton pretreated by cationic starch with lower viscosity and high DS showed perfect level dyeing and high dye fixation which was even higher than that of conventional dyeing. Not only dye utilization efficiency was enhanced, but also pollution from salt reduced greatly. Besides, satisfactory wash fastness and rub fastness were also obtained. And both the small amount of cationic hydrolyzed starch used and continuous utilization of it reduced cost. So cationic hydrolyzed starch may be a possible substitute for salt and show promising use in reactive dyeing.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (NSFC No.20576015).

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