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Novel Green Dyeing Process of Soybean Protein/Poly(vinyl alcohol) Blend Fibre

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Abstract

A water-soluble chitosan derivative N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride (HTCC) was prepared and used for the modification of soybean protein/poly (vinyl alcohol) blend fiber (SPF). The dyeing properties of modified SPF with Cibacron FN series reactive dyes were discussed in relation to a salt-free and alkaline/acidic denaturalization dyeing bath (green dyeing process). Results showed that dye exhaustion in the green dyeing process was obviously higher than that in the conventional dyeing process, despite the addition of a large amount salt in the latter case. However, the washing fastness of SPF treated with HTCC in the green dyeing process was inferior to that of untreated SPF in the conventional dyeing process. COD (chemical oxygen demand) values of the green dyeing process effluent were found to be decreased compared with conventional dyeing effluent, which indicated that the green dyeing process could decrease the amount of toxicity of dyeing effluent remarkably.

Key words: water-soluble chitosan derivative, soybean protein/poly (vinyl alcohol) blend fiber, reactive dyes, salt-free dyeing, denaturalization bath.

Introduction

Soybean protein/poly(vinyl alcohol) blend fibre, hereinafter referred to as soybean protein fibre (SPF), is made by the grafting copolymerization of modified globular protein extracted from soybean meal and nitrile/hydroxyl-containing polymer (polyvinyl alcohol) and then wet spinning [1]. The fibre is valued for its soft handle, excellent wet permeability and warmth retention. In essence, SPF consists of 20% soybean protein and 80% poly(vinyl alcohol) [2]. Reactive dye is widely applied for the dyeing of SPF [3]. In general, the fixation of reactive dye is only 60 - 70%, and then the unfixed dye is released as wastewater. In addition, the dyehouse effluent contains about 30 - 100 g/l electrolyte (sodium sulphate or sodium chloride) used to promote dyeing [4]. A large quantity of salts and dyes in the effluent causes water pollution and upsets the biological equilibrium. Cationization of the fabric surface is an effective way to reduce pollution [5 - 7]. Chitosan, a cationization polymer, has received much attention due to its biodegradability, non-toxicity and antimicrobial activity in recent years [8 - 10]. However, the application of chitosan in textile is limited due to its poor solubility above pH 6.5 [11]. Researchers have focused on the preparation of soluble chitosan derivatives in water over a wide pH range [12, 13].

As is well known, hydrolyzed reactive dye has low affinity to cotton fibre be-

cause of its low physical attraction to cotton fibre. But in an acidic bath some kinds of hydrolyzed reactive dye has high affinity to nylon, wool and SPF because of the additional ionic attraction between the NH_3^+ group of these fibres and SO_3^- group of hydrolyzed reactive dyes [14, 15].

In this study, N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride (HTCC), was prepared by the reaction of chitosan with glycidyl trimethyl ammonium chloride (GTMAC) (*Scheme 1*). The SPF treated with HTCC was dyed with reactive dyes in salt-free and alkaline/acidic denaturalization dyeing bath. The dyeability and washing fastness properties of SPF treated with HTCC and COD (chemical oxygen demand) of the effluent were evaluated.

Experimental

Materials

Pure soybean protein/poly (vinyl alcohol) blend fibre yarn (14.6 tex) was provided by Wuxi Constant Field Textile Co., LTD. (Jiangsu, China). Chitosan, degree of deacetylation 90%, molecular weight about 1.0×10^5 , was obtained from Zhejiang Golden Shell Biotch. Co., LTD. (China). Glycidyl trimethyl ammonium chloride (GTMAC) was supplied by Adamas-beta Reagent LTD. (Shanghai, China). All chemicals used for the following investigations were purchased from Sinopharm Chemical Reagent Co., LTD. (China) and were of analytical grade. Reactive dyes C.I. Reactive Red

238, C.I. Reactive Yellow 206 and C.I. Reactive Blue 235 were obtained from Ciba Specialty Chemicals Company. All the reactive dyes used were bifunctional reactive with the monofluorotriazine and modified cvinyl-sulfone bifunctional reactive groups.

Synthesis and characterization of HTCC

HTCC was prepared by a modified method of Sang-Hoon et al [12]. The chitosan (6 g) was dispersed in isopropanol (60 ml) at 80 °C. GTMAC (16.8 g) was added in three portions (5.6 g each) at 2 h intervals. After 10 h, the clear and yellowish reaction solution was poured into cold acetone (250 ml) while stirring and kept in a refrigerator overnight. The next day, acetone was decanted and the remaining gel-like product was dissolved in MeOH (100 ml). The solution was precipitated in 4:1 acetone-ethanol (250 ml). The white product was collected by filtration and further purified by washing with hot EtOH using a Soxhlet extractor for 24 h. The final product was vacuum dried at 60 °C.

Infrared spectra of chitosan and HTCC were recorded on a Nicolet Nexus-670 FT-IR spectrophotometer (USA) at room temperature by the KBr squashed method.

Degree of quaternization (DQ)

The DQ of the HTCC was determined by titrating the amount of Cl^- ions on the HTCC with a certain concentration of aq AgNO_3 solution [12]. The value of DQ calculated was 0.90.

Treatment of SPF with HTCC

The SPF yarns (2 g) were immersed in HTCC aqueous solution (3 g/l) for 30 min at room temperature under gentle agitation. Afterwards SPF samples were then passed through a padding mangle to remove excess solution and dried at room temperature to obtain HTCC modified SPF.

Dyeability measurement

Dyeing process

Dyeing was carried out at using a liquor ratio of 30:1 and 3% o.w.f shade.

The dyeing of untreated SPF was commenced at 30 °C and maintained for 30 min. Sodium sulfate (50 g/l) was added twice. Subsequently fixation was conducted for 40 min using sodium carbonate (5 g/l) at 60 °C. (It was known as the conventional dyeing process).

Dyeing of the HTCC treated SPF was commenced at 30 °C and maintained for

30 min. Subsequently fixation was conducted for 40 min using sodium carbonate (5 g/l) at 60 °C. Then the pH value of the dyeing bath was adjusted to 3 ~ 4 by disodium hydrogen phosphate and citric acid buffer solution and dyeing was continued for 60 min. (in a salt-free and alkaline/acidic denaturalization dyeing bath, also known as the green dyeing process).

After dyeing, all the dyed samples were rinsed in hot water and soaped in a solution containing a nonionic surfactant (2 g/l) at 90 °C for 20 min at a liquor ratio of 1 : 25. The samples were removed, rinsed thoroughly in hot tap water and air dried (see *Figure 1*).

Dye exhaustion and fixation measurement

The exhaustion and fixation of dyes on SPF fibre were calculated by measuring the absorbance of the residual bath liquor. The percentage of dye bath exhaustion (E in %) and fixation (F in %) was

calculated according to *Equation 1* and *2*, respectively,

$$E\% = \left(1 - \frac{A_1}{A_0}\right) \times 100\% \quad (1)$$

$$F\% = \frac{A_0 - A_1 - A_2}{A_0} \times 100\% \quad (2)$$

where, A_0 is the absorbance of the initial dye solution, A_1 the absorbance of the dye solution after the dyeing process and A_2 is the absorbance of the soaped dye solution. It was determined using a WFZ-26A UV-VIS spectrophotometer (Tianjin Tuopu World Science and Technology Co. Ltd., China).

Cross-section observation

The cross-section of the dyed HTCC treated SPF with a thickness of 1 μm was prepared using an Y172 fibre microtome (Changzhou Second Textile Instrument Factory Co. Ltd., China). Images of the cross-section were obtained at 400 \times magnification using a BP103 light microscope (Shanghai Optical Instrument Factory, China).

Washing fastness measurement

Washing fastness was evaluated according to the respective international standards: fastness to wash, ISO 105-C06: 1994/Cor.2:2002(E). It was carried out by means of a SW-12A II washing fastness tester (Wenzhou Darong Textile Instrument Co. Ltd., China).

Surface morphology observation

The surface morphology of the untreated and treated SPF was observed with a QUANTA200 Scanning electron microscopy by FEI Company (Hillsboro, America).

COD Determination

COD was measured according to ISO6060–1989 (Water quality-Determination of the chemical oxygen demand-Dichromate method). The COD was measured in aqua systems after the dyeing and washing processes.

Results and discussion

Preparation and characterization of HTCC

HTCC was prepared by the reaction of chitosan with GTMAC in a neutral condition (see *Figure 2*). The FTIR spectrum of chitosan and HTCC are shown in *Figure 3*.

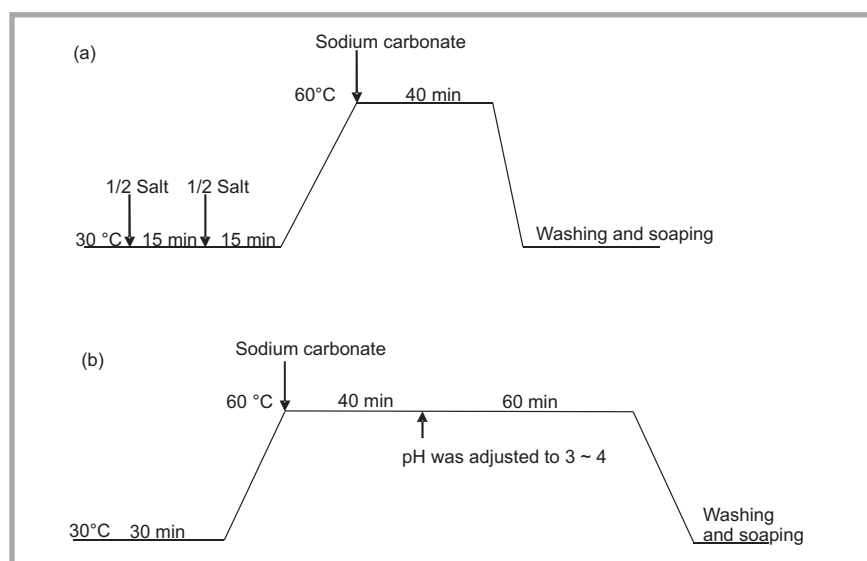


Figure 1. Dyeing process for (a) untreated SPF and (b) treated SPF.

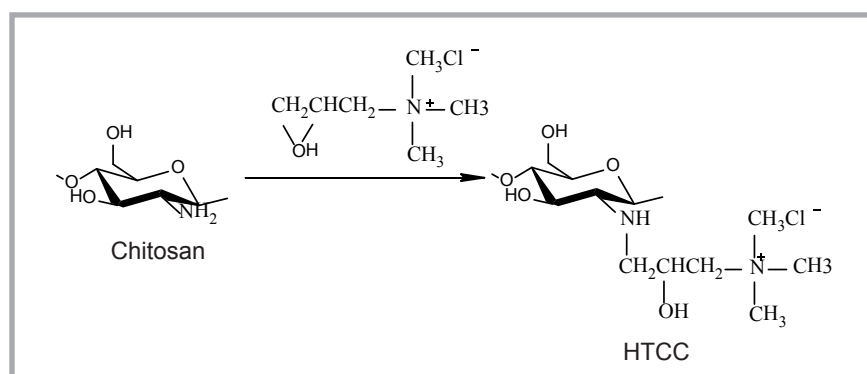


Figure 2. Synthesis of HTCC.

Figure 1.a shows the basic characteristics of chitosan at: 3423 cm^{-1} (O-H stretch), 2925 cm^{-1} (C-H stretch), 1155 cm^{-1} (bridge-O-stretch), 1078 cm^{-1} (C-O stretch) and 895 cm^{-1} (C-O-C stretch of the pyranose ring) [16]. Peaks at 1633 cm^{-1} , 1590 cm^{-1} and 1407 cm^{-1} were assigned to amide I and, II and III bands, respectively. It could be seen that the spectrum of HTCC was similar to that of chitosan but there existed some differences. For HTCC (**Figure 1.b**) a characteristic peak was observed at 1479 cm^{-1} corresponding to C-H bending of the trimethyl ammonium group. Furthermore N-H bending (1590 cm^{-1}) of the primary amine disappeared. It could be that the amino groups of chitosan were substituted by quaternary ammonium salt groups [11].

SEM analysis

SEM observations yielded information about the treatment effects of HTCC on the SPF surface. **Figure 4** illustrates SEM micrographs of untreated SPF (**Figure 4.a**) and HTCC treated SPF (**Figure 4.b**). The SEM image in **Figure 4.a** demonstrated the smooth surface of untreated SPF. **Figure 4.b** shows SEM micrographs of SPF treated with HTCC and depicts a continuous coating layer on the surface of HTCC treated SPF, which indicates a considerable presence of HTCC.

Dyeability analysis

Dyeing properties of SPF treated with HTCC in the green dyeing process and untreated SPF in the conventional dyeing process were shown in **Table 1**.

It can be clearly seen that the dyeing exhaustion and fixation of SPF treated with HTCC in the green dyeing process were much higher than those of untreated SPF in the conventional dyeing process (**Table 1**). Especially for C.I. Reactive Red 238 and C.I. Reactive Yellow 206, complete dye bath exhaustion was almost achieved at the end of dyeing. The increase in values of E% and F% for SPF treated with HTCC in the green dyeing process was associated with two main reasons: Firstly the HTCC could introduce quaternary ammonium groups to the SPF surface, and the zeta potential values of treated SPF increased, and consequently SPF treated with HTCC could adsorb reactive dyes in salt-free dyeing process. Secondly the hydrolyzed reactive dyes used in the experiment had

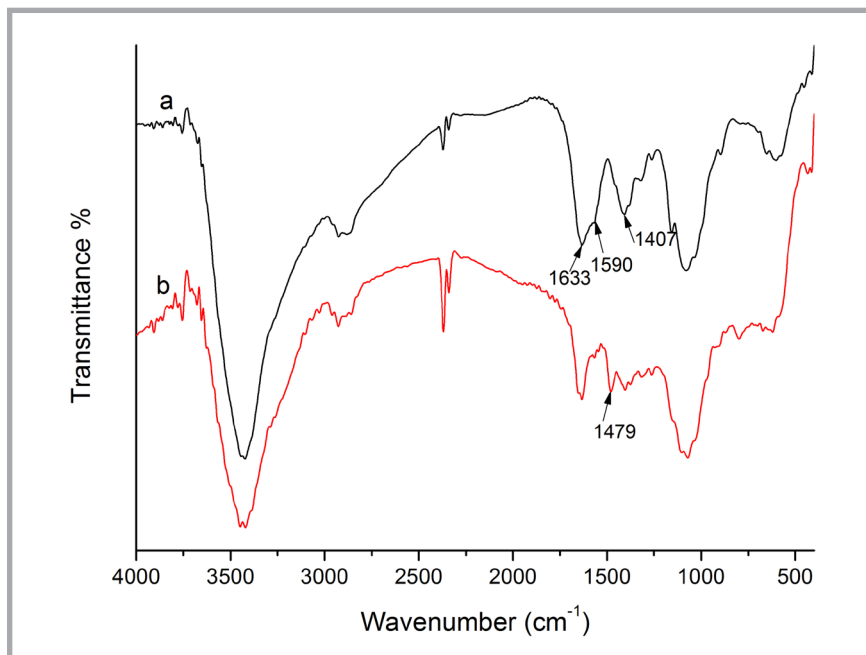


Figure 3. FTIR spectra for chitosan (a) and HTCC (b).

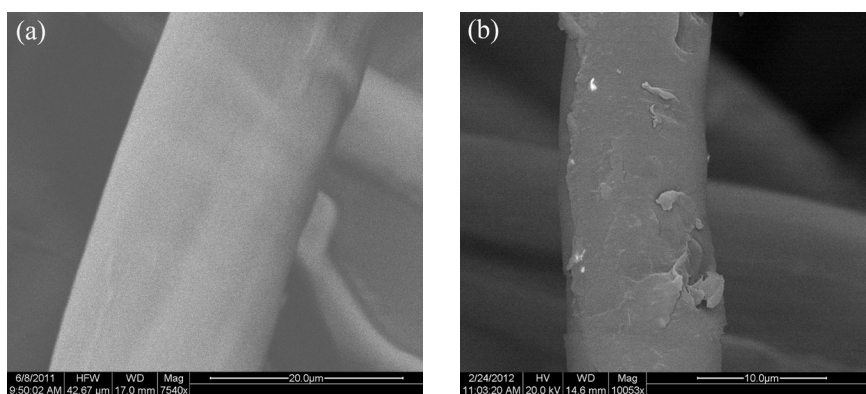


Figure 4. SEM images of the surface morphology of untreated SPF (a) and HTCC treated SPF (b).

Table 1. Comparison of the dyeing properties of SPF treated with HTCC in the green dyeing process and untreated SPF in the conventional dyeing process.

Dyestuff	Sample	E, %	F, %
C.I. Reactive Red 238	Untreated SPF	70.75	60.90
	SPF treated with HTCC	98.30	91.73
C.I. Reactive Yellow 206	Untreated SPF	64.50	51.25
	SPF treated with HTCC	96.73	80.72
C.I. Reactive Blue 235	Untreated SPF	62.69	41.05
	SPF treated with HTCC	91.05	62.09

good dyeability on SPF in acidic conditions. When sodium carbonate was added to the dye solution, some reactive dyes were hydrolyzed and showed very low substantivity to SPF in the alkaline bath. But if the aqueous alkaline bath was adjusted to an acidic pH value, the hydrolyzed reactive dyes could react with the NH_3^+ groups of SPF in acidic conditions, forming ionic linkage [15]. In acidic conditions the dyeing sites on the SPF with

hydrolyzed reactive dyes, i.e. the positively charged groups (NH_3^+), increased as the pH decreased, thereby adsorbing more hydrolyzed reactive dyes. When the pH value was adjusted to 3 ~ 4 below the isoelectric point (pI) of SPF, the percentage of dye exhaustion was evidently further increased. The higher dyeing exhaustion of reactive dyes on SPF treated with HTCC in the green dyeing process was of great benefit in avoiding the large

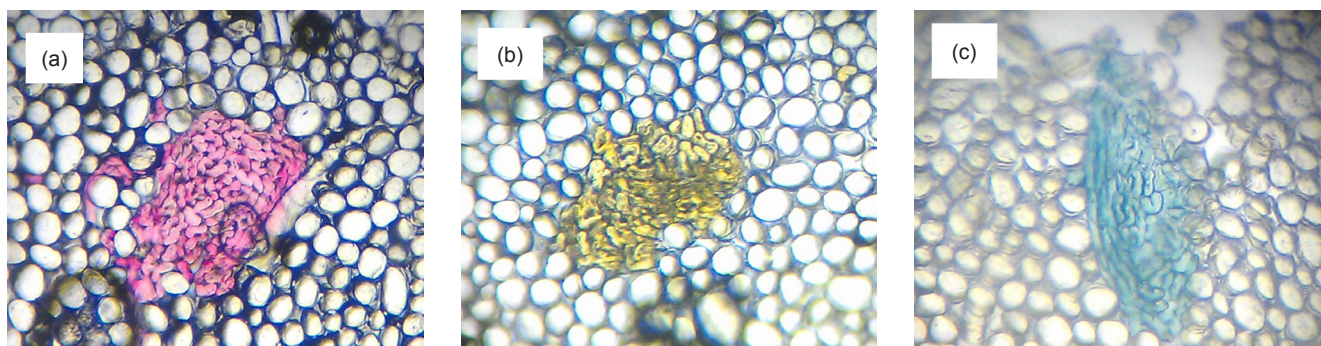


Figure 5. Microscopic photos of SPF treated with HTCC dyed with C.I. Reactive Red 238 (a), C.I. Reactive Yellow 206 (b) and C.I. Reactive Blue 235 (c) in the green dyeing process.

volumes of salt and dyes frequently present in dyehouse effluent.

Penetration ability of reactive dyes

Microscopic photos of the cross-section of dyed SPF treated with HTCC in the green dyeing process are presented in **Figure 5**. When SPF treated with HTCC was dyed with C.I. Reactive Red 238, C.I. Reactive Yellow 206 and C.I. Reactive Blue 23 in the green dyeing process, the inner part of SPF yarns was all coloured, indicating the good penetration of dye. This suggested that the pretreatment of SPF with HTCC and alkaline/acidic denaturalization dyeing bath did not influence dye penetration in the fiber and ring dyeing did not occur. It can be deduced that pretreatment with HTCC and alkaline/acidic denaturalization dyeing bath was suitable for SPF in application.

Washing fastness

The washing fastness of reactive dyes on SPF treated with HTCC in the green

dyeing process and untreated SPF in the conventional dyeing process is shown in **Table 2**. It is shown that the washing fastness of SPF treated with HTCC in the green dyeing process was lower than that of untreated SPF in the conventional dyeing process, especially the change in the shade and staining of adjacent cotton, both being assessed lower than the values of untreated SPF. The main reason is the formation of ionic bonds between the hydrolyzed reactive dyes and SPF treated with HTCC. Further work should be focused on the improvement of the washing fastness of SPF treated with HTCC in alkaline/acid denaturalization bath.

COD_{Cr} values of dyeing effluent

COD is an important index for the assessment of organic pollution in an aqueous system. The larger the COD value is, the more serious the organic pollution of the water body is. The conventional method for COD determina-

tion - K₂Cr₂O₇ is accurate, reliable and reproducible. COD_{Cr} values of green process dyeing effluent and conventional dyeing wastewater are given in **Table 3**. From the tables it can be seen that COD_{Cr} values of green process dyeing effluent were much lower than those of conventional dyeing effluent. The reduction in (COD_{Cr}) values of green process dyeing effluent could be associated with the absence of salt and the good dyeability of hydrolyzed reactive dyes on SPF treated with HTCC in acidic conditions. The results indicate that the green dyeing process could reduce the burdens of follow-up dyeing wastewater treatment and be beneficial to environment protection.

Conclusions

A water-soluble chitosan derivative (HTCC) was prepared by quaterisation. The dyeing properties of SPF treated with HTCC in salt-free and denaturalization dyeing bath were evaluated using Cibacron FN series reactive dyes. The dye exhaustion of reactive dyes on SPF treated with HTCC in the green dyeing process was higher than that on untreated SPF in the conventional dyeing process. The higher dye exhaustion on SPF treated with HTCC was considered to result from the formation of ionic bonds between the cationic groups of HTCC and anionic groups in the dye and the good dyeability of hydrolyzed reactive dyes on SPF in acidic conditions. The washing fastness of SPF treated with HTCC was inferior to that of untreated SPF. Further work is required to improve the washing fastness of SPF treated with HTCC in the green dyeing process. In comparison with conventional dyeing effluent, the COD_{Cr} value of green dyeing process effluent decreased for all the reactive dyes. This green dyeing process would solve the

Table 2. The washing fastness of reactive dyes on SPF treated with HTCC in the green dyeing process and untreated SPF in the conventional dyeing process.

Dyestuff	Sample	Change	Staining	
			Cotton	Wool
C.I. Reactive Red 238	Untreated SPF	4 ~ 5	2 ~ 3	4 ~ 5
	HTCC treated SPF	3 ~ 4	1	4
C.I. Reactive Yellow 206	Untreated SPF	4 ~ 5	4 ~ 5	4 ~ 5
	HTCC treated SPF	2 ~ 3	2	4 ~ 5
C.I. Reactive Blue 235	Untreated SPF	4 ~ 5	4 ~ 5	4 ~ 5
	HTCC treated SPF	3 ~ 4	2	4

Table 3. Comparison of COD_{Cr} in green dyeing process effluent and in conventional dyeing effluent.

Dyestuff	Dyeing effluent	COD _{Cr} , mg.L ⁻¹
C.I. Reactive Red 238	Conventional process	4396
	Green process	684.3
C.I. Reactive Yellow 206	Conventional process	5561
	Green process	769.2
C.I. Reactive Blue 235	Conventional process	7459
	Green process	1006

lower percent of dye utilization and the serious environment pollution problem caused by high salt dosages and residual dyes in dyeing solution.



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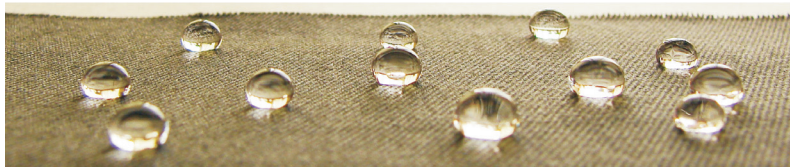
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