Structure and properties of cotton fabrics treated with functionalized dialdehyde chitosan

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ABSTRACT

In this research, modified cotton fabrics were prepared by pad-dry-cure technique from the aldehyde chitosan solution containing 3-aminopropyltriethoxysilane (APTES) and 1,2-ethanediamine (EDA) respectively. The structural characterization of the modified cotton fabrics was performed by attenuated total reflection ATR, scanning electron microscopy (SEM) and thermogravimetry (TG) analysis and physical mechanical properties were measured. The adsorption kinetics of modified cotton fabrics were also investigated by using the pseudo first-order and pseudo second-order kinetic model. The dyeing rate constant k_1, k_2 and half adsorption time $t_{1/2}$ were calculated, respectively. The results show that the mechanical properties of different modified cotton fabrics were improved, and the surface color depth values (K/S), UV index UPF and anti-wrinkle properties were better than those of untreated cotton. Dyeing kinetics data at different temperatures indicate that Direct Pink 12B up-take on the modified cotton fabrics fitted to pseudo second-order kinetic model.
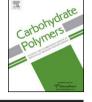
1. Introduction

Chitosan, the cationic (1–4)-2-amino-2-deoxy-D-glucan, is industrially produced from chitin of marine origin (Muzzarelli, 2012; Muzzarelli et al., 2012). Due to its excellent forming film characteristics, nontoxic, environment-friendly, low-cost and high-efficiency, high contents of amino and hydroxyl functional groups in the chains, chitosan has attracted great attention as a useful bio agent in textile dyeing and finishing (Janjic et al., 2009; Lim & Hudson, 2004; Liu, Nishi, Tokura, & Sakairi, 2001).

Chitosan can be oxidized by ozone (Yue, He, Yao, & Wei, 2009), H_2O_2 (Tian, Liu, HU, & Zhao, 2003), $CrO_3 + HClO_4$, H_2O_2/Na_2WO_4 (Terada et al., 2003), $NaIO_4$ (Bouhadir et al., 2001), nitrous acid (HNO_2) (Terada et al., 1999), and 2,2,6,6-tetramethylpiperidinyl (TEMPO) radical in the presence of NaOCl and NaBr (Fan, Saito, & Isogai, 2008; Muzzarelli, Muzzarelli, Cosani, & Terbojevich, 1999). Of these, the use of periodates selectively cleaves the 2,3 C—C bond and converts chitosan into a dialdehyde derivative has been extensively investigated (Vold & Christensen, 2005). Cortesi, Nastruzzi, and Davis (1998) reported the cross linking of gelatin with oxidized sugars, where microspheres and disks were prepared by this method. Similarly, Wang and Hon (2003) used oxidized sugars to prepare crosslinked chitosan-PEG membranes and crosslinked N-alkylated chitosan membranes, respectively. They proposed that Schiff base formation between the aldehyde groups from oxidized sugar with the amine groups from gelatin was responsible for the hydrogel formation.

The cotton fabric characteristically exhibits excellent physical and chemical properties in terms of water absorbency, dyeability and stability. Their increased demand and popularity are for multi-function, bright color, excellent color fastness, water-fast, simple application techniques and low energy consumption (Franklin & Rowland, 1983; Xiao, Zhang, Yang, & Huang, 2007). For realizing these purposes, many efforts have been made. Among of them, modifications have been prevalently employed in the past years (Cheng & Biswas, 2011; Harifi & Montazer, 2012; Lim & Hudson, 2004). However, the modification technology of cotton fabrics has some problems, which restrained their application, for example, excessive cost, wearability of dyed fabrics (moisture, air permeability and tear strength) degeneration, health and safety of modification technology, etc. In this work, novel methods to modify cotton fabrics were proposed by using ecologically sustainable and cheap chitosan oxidation. Firstly, chitosan were oxidized selectively with periodates, then the modified cotton fabrics were prepared by using oxidation chitosan and nitrogen-containing reagents including 3-aminopropyltriethoxysilane (APTES) and 1,2-ethanediamine (EDA) respectively. The structure of modified cotton fabrics was characterized by ATR, SEM and TG-DSC. The physical

mechanical and dyeing properties were measured, and the dyeing kinetic experiments of modified cotton were carried out. The adsorption behaviors of the modified cotton for Direct Pink 12B were analyzed by fitting experimental data in various kinetics models such as the pseudo-first-order kinetic model and pseudo-second-order kinetic model.

2. Experimental

2.1. Materials

Desized, scoured and bleached cotton fabrics were obtained from Jinqiu Textile and Finishing Company, Shaoxing, China.

2.2. Chemical agents

Chitosan (degree of deacetylation 96.31%, MW = 7.9×10^5 Da) was purchased from Zhejiang Jinke Bio-tech Co., Ltd. (Zhejiang, China). Starch, sodium periodate (analytical pure) and sodium borohydride were purchased from Guoyao Chemical Co.; 3-aminopropyltriethoxysilane (APTES) was supplied by Yancheng Renbo Chemical Co.; acetone, ethylene glycol, acetic acid, hydrochloric acid, phosphoric acid, orthoboric acid and 1,2-ethanediamine (EDA) were of analytical grade and purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Sodium hydroxide was of analytical grade, and was used without further purification. The direct dyes Pink 12B (C.I. Direct Red 31) were supplied by Zhejiang Longsheng Dye Chemical Co., Ltd. (Shangyu, China).

2.3. Preparation of aldehyde chitosan

Aldehyde chitosan was performed following the conditions adopted previously for chitosan (Vold & Christensen, 2005): 3 g polysaccharides were added in 100 ml of aqueous solution containing 0.3 mol l^{-1} sodium periodate under stirring (molar ratio = 1.613:1) at 30 °C in a lightproof condition. After 2 h, 20 ml of 0.1 mol l^{-1} solution of ethylene glycol was added with the purpose of halting reaction and removing the excess of unreacted periodate for 0.5–1 h. Then 100 ml acetone was poured into the reaction mixture solution to precipitate the product, 1–3 h. The precipitate was collected and dried. At last, the oxidation dialdehydes chitosan was obtained and denoted as OCS.

2.4. Modification of cellulose fabrics

Modification of cotton fabrics with oxidized chitosan solution was carried out using pad-dry-cure technique. Cotton fabrics were first impregnated in aqueous solution of 5 g l^{-1} of oxidized chitosan solution containing 10 g l^{-1} of APTES and 10 g l^{-1} of EDA respectively, 30 min, with a liquor ratio of 1:50 at ambient, and then padded through two dips and two nips to reach an average wet pickup of 80%, dried at 80 °C for 3 min. The curing was done at 120 °C for 5 min. After that, the treated sample was immersed in 10 g l^{-1} sodium borohydride for 30 min to reduce the forming Schiff base. And finally the treated fabrics were washed with water and air-dried in a conditioning room (25 °C, 65% R.H.) for 24 h. The modified cotton fabrics were obtained, and denoted as OCS, OCS + APTES, OCS + EDA respectively. The scheme of cross-linking cotton with aldehyde chitosan and EDA, APTES respectively are shown in Fig. 1.

2.5. Dyeing procedure

The cotton fabric was introduced into a dyebath containing 2% (omf) Direct Pink 12B, 20 g l^{-1} sodium sulfate, a liquor ratio of 50:1. The dye bath was raised to 70 °C and maintained at the temperature

for 60 min. Finished samples were thoroughly washed with warm and cold water to remove un-reacted and unfixed materials, dried and conditioned before testing.

2.6. Dyeing kinetics

0.3 g modified fabrics and control samples were dyed with Direct Pink 12B in a beaker with frequent shaking according to the adsorption process as mentioned above. After each interval, 5 ml of the bath was taken into test tubes and diluted with distilled water to 50 ml to measure its absorbance at 520 nm. Dye exhaustion (E) was determined from a visible absorbance recorded on UV–visible spectrophotometer at the λmax of each dye solution before (A_0) and after dyeing (A_1) as described in Eq. (1)

$$E\% = \frac{A_0 - A_1}{A_0} \times 100\% \tag{1}$$

where A_0 and A_1 absorbance before and after dyeing with direct pink 12B, the amount of dye on fiber were calculated as follows:

$$q = \frac{C_0 \cdot E\% \cdot V}{1000 \cdot W} \tag{2}$$

where C_0 (mg l^{-1}) are the initial concentration of Direct Pink 12B, respectively; V (ml) is the volume of solution, and W (g) is the dry weight of fiber.

To examine the mechanism of the adsorption process, the pseudo-first-order equation, the pseudo-second-order equation and particle diffusion equation based on adsorption equilibrium the amount of dye on fiber may be expressed in the form as Eqs. (3)–(5) (Liang, Feng, Meng, & Liang, 2005).

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1 t}{2.303} \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

$$q_t = k_i t^{1/2} + C \tag{5}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are respectively the amount of dye on fiber at dyeing equilibrium and the amount of dye on fiber at time t (min), k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are respectively the kinetic rate constants for the pseudo-first-order equation and the pseudo-second-order equation. The slopes and intercepts of plots of $\ln(q_e - q_t)$ versus t are used to determine the pseudo-first-order rate constant k_1 and q_e. The slopes and intercepts of plots of t/q_t versus t are used to calculate the pseudo-second-order rate constant k_2 and q_e. k_i and C are respectively rate constant and constant for the particle diffusion equation (Stefancich, Delben, & Muzzarelli, 1994).

2.7. Measurement of color strength

Spectral reflectance factors (taken between 400 and 700 nm wavelengths in 20 nm increments) of the samples were measured using a Datacolor7000A reflectance spectrophotometer (Data color International Ltd., UK) interfaced to a computer. Each fabric sample was folded twice to give a total of four layers. Under illuminant D65 using the 10° standard observer, the relative color strength (K/S value) were automatically calculated from reflectance factors R of the dyed fabrics at the maximum absorbance wavelength by the software using the Kubelka–Munk equation (6).

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \tag{6}$$