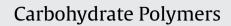
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Chemical modification of cotton fabrics for improving utilization of reactive dyes

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ABSTRACT

The cotton fabric was chemically modified with the acrylamide through Michael addition reaction and Hoffman degradation reaction. And the optimum chemical modification conditions were determined. The molecular structure of the modified cotton fabric was identified by Fourier transform infrared spectroscopy (FTIR). The structures of both the raw and modified cotton fabrics were investigated by X-ray diffraction and scanning electronic microscopy. The raw and modified cotton fabrics were dyed using commercial reactive dyes with vinyl-sulfone groups. The results showed that the total dye utilization of modified cotton fabrics in the salt-free dyeing was higher than that of raw cotton fabrics in the conventional dyeing. And the color fastness properties and tear strength of modified fabrics were both satisfactory.

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1. Introduction

The cotton fabric characteristically exhibits excellent physical and chemical properties in terms of water absorbency, dyeability and stability. Reactive dyes are often referred to as the king of dyes for cotton fabrics dyeing system. Their increased demand and popularity are for bright color, excellent color fastness, water-fast, simple application techniques and low energy consumption (Aksu & Tezer, 2000). However, it is necessary to use a large amount of salt (sodium chloride or sodium sulphate) to overcome the static repulsion between cotton fabrics and reactive dyes to promote dyeability in the traditional dyeing process. Even so, the reactive dyes are far from ideal because they are difficult to exhaust from the dyebath and the fixation reaction between dye and cotton fabrics is also inefficient. Depending on the different nature of the used dye and fabric, as much as 40-50% of the dye remained in the dyebath effluents (Aksu & DÖnmez, 2005; Jiang et al., 2011). Discharges of high electrolyte concentrations are undesirable since increased salinity of the rivers affects the delicate biochemistry of aquatic life. The residue of dyes and electrolytes has posed a significant environmental hazard.

Therefore, how to improve utilization of the reactive dyes and to reduce or eliminate the amount of electrolyte used in cotton dyeing has been an important problem concerned by many researchers. In the last recent years, there have been many efforts to improve the dyeability of cellulosic fabrics (Burkinshaw, Mignanelli, Froehling, & Bide, 2000; Cheng & Biswas, 2011; Corrales et al., 2007; Feng

0144-8617/\$ - see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.carbpol.2012.08.049 & Chen, 2008; Heinze & Liebert, 2001; Ibrahim, El-Zairy, El-Zairy, Eid, & Ghazal, 2011; Kitkulnumchai, Ajavakom, & Sukwattanasinitt, 2008; Lewis & Lei, 1991; Lewis & Mcllroy, 1997a; Lim & Hudson, 2004; Liu, Yang, Zhang, Liu, & Xiong, 2007; Shin & Yoo, 1998; Wang, Ma, Zhang, Teng, & Yang, 2009; Xie, Liu, & Wang, 2009; Zhang, Chen, Lin, Wang, & Zhao, 2008). Among those efforts, the surface modification of cellulosic fabrics has attracted much attention. The process is primarily to attach the cationic compounds on cotton fabrics by chemical binding or physical adsorption for enhancing the substantivity between anionic dye and cotton. Such treated cotton would be dyeable with reactive dyes under neutral or mildly acidic conditions in the absence of electrolyte in the dyebath (Wang & Lewis, 2002).

But 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, complication of industry dyeing technology (Teng, Ma, & Zhang, 2010; Xu, Renfrew, & Phillips, 2005). Despite all of the above approaches, none has achieved commercial importance (Xu et al., 2005).

Introduction of amine groups into the cellulose structure produces a fiber that may be considered analogous to wool. Wool has a natural substantivity towards anionic dyes (Lewis & McIlroy, 1997b) and the amino group can react more easily with reactive dyes than the hydroxyl group. A novel method to prepare aminoethyl cotton was proposed and investigated by treating cotton fabrics with ecologically sustainable and cheap acrylamide. This method could improve the substantivity of cotton for reactive dyes to achieve the goal of salt-free or low-salt dyeing.

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2. Experimental

2.1. Materials

The cotton fabric used in this work was desized, causticboiled, bleached, weighing approximately 100 g/m^2 . The fabric was washed in the laboratory at $100 \degree \text{C}$ for 60 min using the distilled water. It was then dried at ambient conditions.

2.2. Chemicals

Sodium hydroxide, acrylamide, sodium nitrite, sodium carbonate, sodium chloride, sodium hypochlorite and other chemicals were of laboratory-grade chemicals from Sinopharm Chemical Regent Co., Ltd.

The commercial reactive dye, C.I. Reactive Black 5 and C.I. Reactive Blue 19 were supplied by Shanghai Dyestuff Co., Ltd., China, C.I. Reactive Yellow 176, C.I. Reactive Red 195, were supplied by Zhejiang Longsheng Group Co., Ltd., China. And their structures are given in Fig. A.1.

2.3. Chemical modification of cotton fabrics

The first step was Michael addition reaction. Acrylamide and sodium nitrite (2 g/L) were mixed in an aqueous solution. The pressure on the mangle was adjusted to give 100% wet pickup. Cotton fabrics were dipped and padded twice in the above solution. And then the above cotton fabrics were dipped and padded twice in the aqueous solutions of sodium hydroxide. The two-bath dipping and padding process kept at room temperature. The treated fabric was then subjected to heat treatment at a specific temperature for a certain length of time. After that, it was cooled to ambient temperature, then washed with distilled water, and finally dried in air.

The second step was Hoffman degradation reaction. The treated fabric was immersed in the beaker placed mixture solution of sodium hydroxide and sodium hypochlorite in the proper proportions. Then it was placed in the Thermostatic Water Bath for a specified period of time. After the reaction, the treated fabric was removed, washed with distilled water and dried. The final modified cotton fabric was thus prepared. Details of the conditions used are given in the text.

2.4. Kjeldahl nitrogen determination

The Kjeldahl method was used for analyzing the nitrogen contents of modified cotton fabrics using a Kjeltec 2300 Analyzer (Foss Tecator).

2.5. Characterization

Infrared spectroscopy (IR) experiments of the fabrics were performed using a Nicolet 460 FTIR under standard operating conditions.

The surface morphologies of the untreated and treated cotton fabrics were observed with LEO 1530 scanning electron microscope. All the samples were coated with gold before SEM testing.

The X-ray diffraction (XRD) patterns of the fabrics were measured stepwise in the 2θ between 5° and 60° by a X" Pert PRO diffractometer (PANalytical, Netherlands).

2.6. Dyeing procedures

2.6.1. Dyeing procedure for the modified cotton (aminoethyl cotton)

The dyeing was carried without the addition of salt. The modified cotton fabric was introduced in aqueous bath containing 4% dye (omf, weight percent of dye relative to fiber) at a liquor ratio of 1:30. The temperature was kept at 25 °C. After 30 min, the dyeing temperature was gradually increased to 60 °C in 20 min. Then 20 g/L sodium carbonate was added with stirring and the dyeing process was continued for 60 min. At the end of dyeing process, the dyed fabric was soaped in a solution of a nonionic surfactant (Triton X-100, 1 g/L) at 90 °C for 20 min at liquor ratio 1:30 and then thoroughly rinsed in tap water.

2.6.2. Dyeing procedure for the untreated cotton

The untreated cotton fabric was introduced in aqueous bath containing 4% dye (omf) at a liquor ratio of 1:30. In the dye bath, 25 g/L sodium chloride was added with stirring. The temperature was kept at 25 °C. After 30 min, another 25 g/L sodium chloride was added and the dyeing temperature was gradually increased to 60 °C in 20 min. Then 20 g/L sodium carbonate was added and the dyeing process was continued for 60 min. The dyed fabric was soaped in a solution of a nonionic surfactant (Triton X-100, 1 g/L) at 90 °C for 20 min at liquor ratio 1:30 and then thoroughly rinsed in tap water.

2.7. Determination of dye exhaustion and fixation

The absorbance of the dye solution was measured at λ_{max} before and after the dyeing processes using a Lambda 950 Spectrophotometer (PerkinElmer Co. Ltd.). The percentage of dyebath exhaustion (*E*) was calculated using Eq. (1), where A_0 and A_1 were the absorbance of the dye solution before and after the dyeing process, respectively. And the fixation of the adsorbed dye (*F*) was calculated using Eq. (2) and the total utilization of the original applied dye (*T*) was calculated using Eq. (3), where A_2 was the absorbance of the dyebath after soaping.

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

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

$$T = E \times F \tag{3}$$

2.8. Color yield analysis

The color yield or the color strength expressed as K/S value was calculated from the Kubelka–Munk equation as given below (Eq. (4)), where K is the absorbance coefficient, S is the scattering coefficient, and R is the reflectance ratio measured at the maximum absorbance of dye using a CM-2600d Spectrophotometer (Konica Minolta). After folding each fabric twice, measurements were taken at four different positions on the fabric surface and averaged.

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$
(4)

2.9. Color fastness and tear strength testing

The washing properties were measured by SW-12 (Dongyuan testing Machinery) washing machine according to the standard, ISO 105-C06 (C2S). Meanwhile, the rubbing fastness properties were evaluated according to the standard, ISO 105-X12 on Y571B (Changzhou Textile Instrument Co., Ltd.) rubbing machine.

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