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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

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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)

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

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:

$$q = \frac{C_0 \cdot E\% \cdot V}{1000 \cdot W} \quad (2)$$

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).

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

$$q_t = k_i t^{1/2} + C \quad (5)$$

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).

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

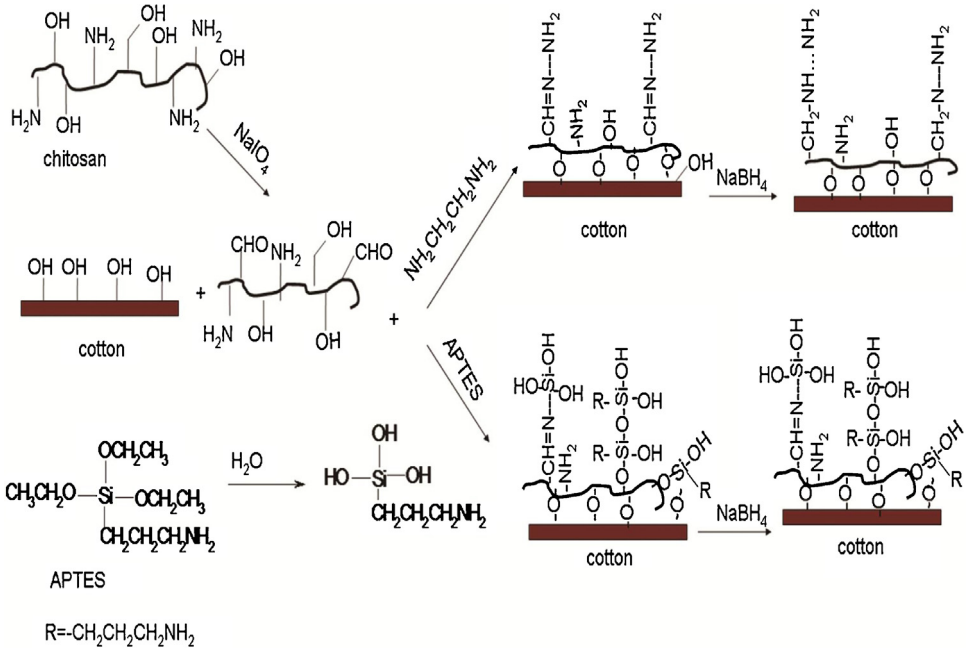


Fig. 1. Scheme of oxidized chitosan crosslinking cotton with EDA and APTES respectively.

where K is the absorption coefficient of the substrate, S is the scattering coefficient of the substrate and R is the reflectance of the dyed fabric at λmax.

2.8. Physical mechanical properties measurement

Cotton fabric samples were air conditioned at 25 ± 2 °C and 65 ± 2% RH for 24 h, and their performance was measured as following methods. Whiteness was determined with a WSB-3A digital fluorescent whiteness meter. Whiteness index of the treated cotton fabrics was measured with Color-Eye 7000A spectrophotometer from Datacolor International Ltd. (UK). The tensile strength of fabrics was measured by YG (B) 026D-250 fabric tensile strength tester (Wenzhou Darong Textile Instrument Co., Ltd., China) in accordance with the method of ISO5081. Six specimens (three for warp and three for filling) were tested at a gauge length of 200 mm with a stain rate of 30 mm min^{-1}. The width of the specimen was 50 mm. The warp tensile strength and elongation at break were determined for the untreated and treated fibers according to the ASTM D5035 strip test.

2.9. UV protection and resistant to crease properties

UV Transmittance Analyzer, UV-912E tester (Wenzhou Darong Textile Instrument Co., Ltd., China), measured ultraviolet protection factor (UPF), T (UVA), and T (UVB). The UPF was calculated by using Eq. (7).

$$\mathrm{UPF} = \frac{\int_{290}^{400} E_\lambda \times S_\lambda \times d\lambda}{\int_{290}^{400} E_\lambda \times S_\lambda \times T_\lambda \times d\lambda} \quad (7)$$

where S_λ is erythema action spectrum, E_λ is solar irradiance, d_λ is wavelength interval in nm (Tragoonwichian, O'Rear, & Yanumet, 2009), T_λ is the spectral transmittance of the specimen.

Wrinkle recovery angle (WRA) of the cotton fabrics were measured according to AATCC Standard Test Method 66-2008. Ten specimens (five for warp and five for filling) were tested for WRA.

2.10. Product characterization

ATR-FTIR transmission spectra were acquired in the range of 4000–650 cm^{-1} using a Fourier Transform Infrared spectrometer (FT-IR) with a Flat-plate Attenuated Total Reflectance (ATR) (Thermo Nicolet, USA).

The SEM images of modified cotton were taken using a scanning electron microscope (FEI Quanta 200 scanning electron microscope, USA). Samples were coated an approximate layer thickness of 15 nm with gold, and the SEM images were taken at an accelerating voltage of 10 kV.

Thermal stability of the control and modified cotton fabrics was analyzed using a thermogravimetric analyzer (Type STA-449C; NETZSCH Instrument Co., Ltd.; Germany) in N_2 atmosphere. The temperature ranged from 20 to 650 °C at a scanning rate of 10 °C min^{-1}.

3. The results and discussions

3.1. ATR spectroscopy

The ATR spectra of untreated cotton and modified cotton are shown in Fig. 2. A strong O—H absorption at 3338 cm^{-1} with a broad peak appeared in ATR spectrum of the untreated cotton. The bands at 2897 cm^{-1} were assigned to C—H bonds which normally appear on cotton surface. The band at 1320 cm^{-1}, 899 cm^{-1} is assigned to C═O, C—O group (Tragoonwichian et al., 2009). Influenced by the amounts of C═O groups in OCS, the νC═O absorption due to the conjugated carbonyl (amide and carboxyl) groups was clearly detected at 1627 cm^{-1} from the OCS treated cotton surface. The band at 1245 cm^{-1} is assigned to the C—O stretching of an ester (Monier & El-Sokkary, 2012). The spectral intensity in the ranges remained essentially unchanged as shown by the spectra of the fabrics treated with OCS. Strong absorptions at 2926 and 2854 cm^{-1} in the spectrum of OCS + EDA modified cotton were assigned to the asymmetric and the symmetric vibrations of-CH_2-from EDA in modified cotton.

For the OCS + APTES treated cotton in Fig. 2, there is the band at 3500–3000 cm^{-1}, 2980–2800 cm^{-1}, 1433–1428 cm^{-1}, which is

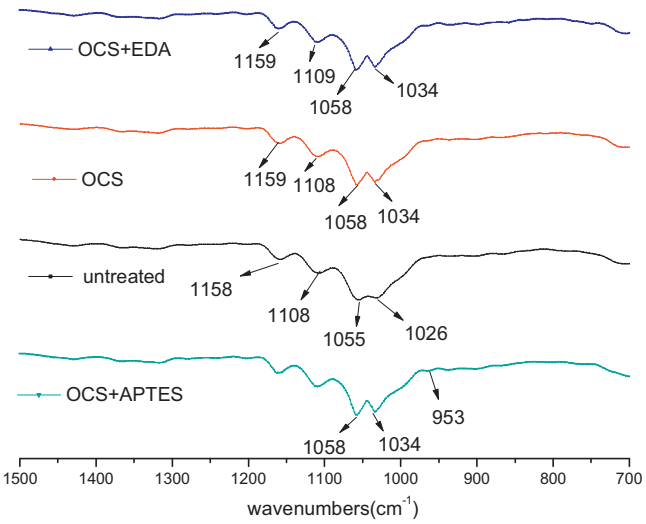


Fig. 2. FT-ATR of untreated and modified cotton.

due to characteristic of hydrogen bonded O—H stretching, C—H stretching and C—H wagging of cellulose, respectively. Compared with the untreated cotton fabrics, the characteristic peaks of the silica sol deposition show small but significant on the OCS + APTES modified cotton. Deposition of the silica film on the surface of cotton fibers has been confirmed by the presence at around 1200, 953, and 796 cm^{-1} of absorption bands assigned to Si—O stretching vibration shoulder, Si—OH stretching, and Si—O—Si symmetric stretching, respectively (Tragoonwichian et al., 2009).

3.2. Morphology of the cotton fabrics

SEM analysis has been performed in order to assess the morphology of the fibers after the different ways of treatments. The images of untreated and OCS, OCS + APTES, OCS + EDA treated cotton fibers are shown in Fig. 3(a)–(d), respectively. The SEM image of the surface of untreated cotton (Fig. 3a) revealed characteristic parallel ridges and grooves (Wang, Fan, Gao, & Chen, 2006). The image of the OCS treated cotton fibers showed a layer of unevenly OCS polymer deposition (Fig. 3b). The OCS + EDA modified cotton (as shown in Fig. 3c), presented a flatter and smoother surface without pronounced cavities, compared to the untreated cotton. This indicated that the alkali had a peeling effect on the non-cellulosic impurities (Wang et al., 2006). The surface features of the OCS + APTES treated cotton (Fig. 3d) were clearly different from those of the OCS + EDA treated cotton. The surface roughness increases and the presence of a homogeneous thin coating on the single fibers can be noted, which showed the silane couple crosslinking, forming silica network structure and deposition on cotton fibers (Hou, Yu, & Chen, 2010).

3.3. Thermal stability

DSC and TGA curves of untreated samples and modified cotton fabrics with OCS, OCS + APTES, OCS + EDA respectively in nitrogen are shown in Fig. 4.

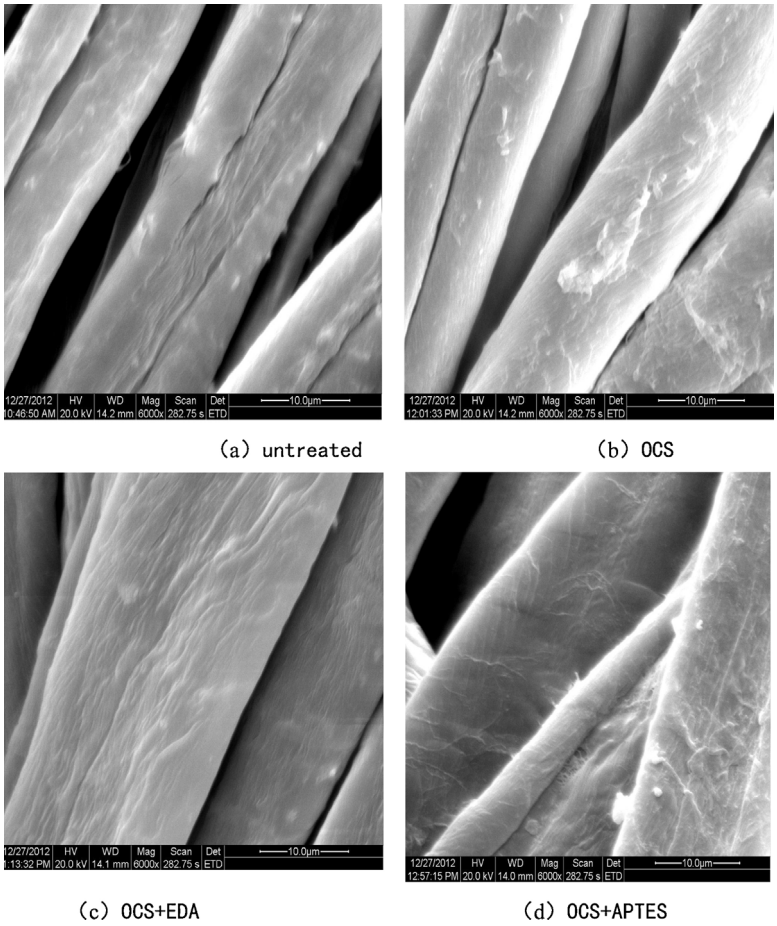
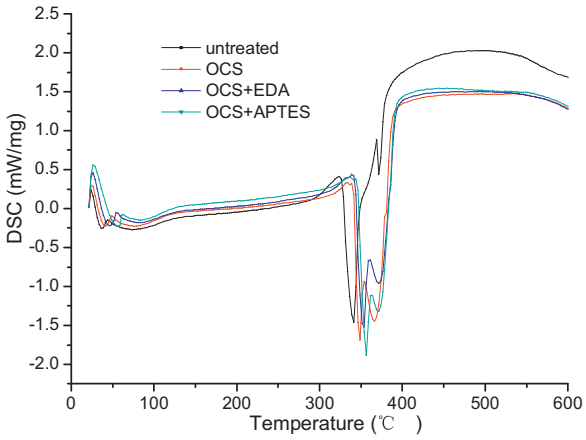
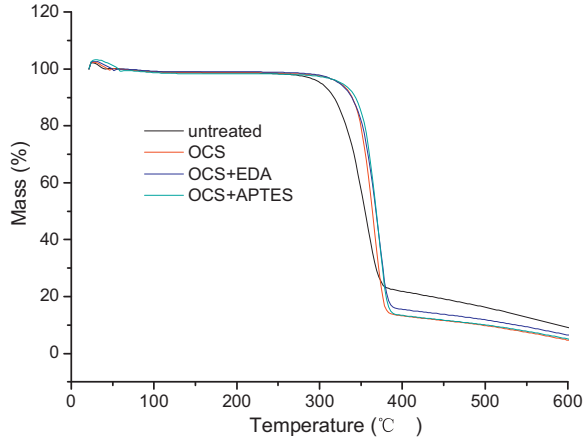


Fig. 3. SEM of untreated and treated cotton fabric samples. (a) untreated; (b) OCS; (c) OCS + EDA; (d) OCS + APTES.



(a) DSC curves of untreated and modified cotton



(b) TG curves of untreated and modified cotton

Fig. 4. Thermal stability of untreated and modified cotton.

The DSC plots of modified cotton fabrics and untreated samples show two endothermic processes (Fig. 4a). The 50–100 °C broad peaks are related to loss of moisture absorbed by the samples during their processing. The endothermic peak in the region 310–350 °C corresponded to segmental motions in modified materials under thermal decomposition, and its shift could be explained by assuming that the untreated and modified cotton were already degraded with a large fraction of oligomers and therefore less energy was necessary for their thermal decomposition. DSC thermograms for the OCS treated cotton showed no apparent change in terms of shape if compared to the corresponding DSC curves for the untreated cotton fabric.

Exothermic peak at around 378 °C only in nitrogen atmosphere was a thermal decomposition event due to a process of crosslinking of the products of carbonization (Bosco et al., 2013; Girardi et al., 2011). Besides, between 323 and 382 °C, the OCS + EDA, OCS + AOTES treated samples exhibited a shoulder endothermic peak, corresponding to the pyrolysis process. Here, the pyrolysis of the OCS + APTES modified cotton shows higher decomposition temperatures and higher weight loss than those of the untreated cellulose. The increase in degradation temperature indicates the strong organic-inorganic phase interactions (probably also the covalent bonding) greatly influencing the thermal resistance. It showed the silane couple crosslinking and forming silica network structure could increase the thermal stability of cotton.

The TGA plots of the treated and untreated cotton fabrics are shown in Fig. 4b (in nitrogen). A small weight loss at about 100 °C corresponded to water release for the initial step. The main pyrolysis phase occurred in the temperature range of 280–350 °C. In this stage, the weight loss was very fast and significant. Most of pyrolysis products were produced in this stage (Lessan et al., 2011). From Fig. 4b, thermal degradation of untreated, OCS, OCS + APTES, OCS + EDA modified cotton is observed at about 341.1, 346.6, 350.3, 349.8 °C respectively. The char pyrolysis occurs at the temperature above 400 °C. The weight losses for untreated, OCS, OCS + APTES, OCS + EDA modified cotton were 93.92, 98.19, 98.93, 97.76% respectively. During this process, the mass decomposition continues to dewater and decarboxylize, releasing more water and carbon dioxide and producing double bond, carboxyl and carbonyl products (Bosco et al., 2013).

3.4. Physical mechanical properties

Table 1 shows those mechanical properties of the untreated and treated fabrics such as strength, elongation at break and whiteness, etc. The tensile strength of the fabric depends on many factors (fabric structure, yarn twist, yarn count, etc.), The tests carried out for OCS, OCS + EDA, OCS + APTES modified cotton showed there were a slight enhancement for both the tensile strength and the elongation at break. This was contrary to the results that crosslinking of cellulose molecules with BTCA caused a decrease in strength in literature (Alimohammadi, Gashti, & Shamei, 2012; Colleoni et al., 2013). This behavior was probably because crosslingkage forming between oxidized chitosan and cotton fiber eliminated the fibers weak binding sites, preventing the fiber breakages which stress assembly caused, thereby enhancing the strength of the fiber. So, oxidized chitosan treatment increases the strength of the treated fabrics.

In fact, for the OCS + APTES modified cotton, a silica layers film formed by APTES hydrolysis and condensation could take place with the number of contact points, increasing substrate rigidity. It was consistent with the results that the TEOS sol–gel treated cotton had maintenance or a slight enhancement of mechanical characteristics with increasing number of silica layers (Colleoni et al., 2013).

Wrinkling is one of the most important disadvantages of cotton fabrics (Colleoni et al., 2013). It was observed that the wrinkle recovery angles (WRA) for treated cotton fabrics with OCS, OCS + EDA, OCS + APTES respectively increased (Table 1). The WRA of the treated fabric remained in the 280°–302° range, which was higher than that of untreated cotton (265°). Cellulose macromolecules are composed of glucose rings which are joined together and hydroxyl groups are protruding from the macromolecular chains providing reactive cross-linking sites (Ibrahim, Amr, Eid, Almetwally, & Mourad, 2013). Cross-linking reactions occur within the accessible regions with hydroxyl groups of cellulose resulting in a better resistance to deformation and improving elastic recovery from deformation (Bajaj, 2002). The cross-linking of the cotton and OCS, the hydroxyl groups of cellulose chains included cross-linking by ester linkages in the less-oriented (paracrystalline) or amorphous regions of cellulose, which improves the crease resistance of the fabrics.

UPF and percentage of transmission are main parameters for assessing UV protection ability of the fabric. As shown in Table 1, all the modified cotton fabrics showed an increase in UPF values, compared to the untreated samples. Generally, UPF value of 15–24 is classified as good protection, 25–39 as very good and above 40 as excellent protection against solar UV radiation (Wang & Hauser, 2010). The untreated sample showed a low UPF value at 16.6. The UPF values of modified cotton fabrics with OCS and N containing agent (APTES and EDA) all exceeded 30, having good UV protection

Table 1
Physical mechanical properties of untreated and modified cotton.

Sample	WI[a]	Tensile strength (N)	Elongation at break (%)	WRA[b] (W+F)°	UPF[c]	K/S
Untreated	91.48 ± 4.57	594 ± 29.70	5.63 ± 0.28	265.2 ± 13.26	16.6	11.94 ± 0.60
O-CS	90.76 ± 4.54	595.87 ± 29.79	10.41 ± 0.52	298.15 ± 14.91	39.1	12.68 ± 0.63
O-CS + APTES	91.28 ± 4.56	602.8 ± 30.14	9.76 ± 0.49	301.5 ± 15.08	37.1	13.22 ± 0.66
O-CS + EDA	91.36 ± 4.57	606.57 ± 30.33	10.04 ± 0.50	280.15 ± 14.01	34.3	15.20 ± 0.76

[a] WI, whiteness index.
[b] WRA, recovery angle (warp +filling) (°).
[c] UPF, UV-protection factor.

Table 2
Comparison of the pseudo-first and pseudo-second order constant at different temperature (dye 2%, 20 g l^{-1} Sodium sulfate, liquor ratio of 50:1).

Temp	Samples	Pseudo-first order kinetic model			Pseudo-second order kinetic model				$t_{1/2}$(min)
		q_{exp} (mg g^{-1})	K_1 (min^{-1})	R^2	q_{cal} (mg g^{-1})	K_2*10^{-3} (g mg^{-1} min^{-1})	q_{cal} (mg g^{-1})	R^2	
50 °C	Untreated	7.06	0.015	0.9212	7.28	3.877	7.66	0.9663	33.66
	OCS + APTES	8.18	0.016	0.9519	8.36	3.377	9.02	0.9729	32.84
	OCS + EDA	7.84	0.016	0.9391	8.03	3.089	8.76	0.967	36.97
70 °C	Untreated	9.6	0.021	0.9684	9.67	6.899	9.98	0.9945	14.52
	OCS + APTES	10.92	0.020	0.9855	11.00	5.027	11.52	0.9931	17.27
	OCS + EDA	11.08	0.021	0.9419	11.15	4.497	11.72	0.9906	18.99
90 °C	Untreated	6.81	0.037	0.8792	6.82	18.283	7.20	0.9968	7.60
	OCS + APTES	7.25	0.029	0.9545	7.26	14.548	7.51	0.9975	9.15
	OCS + EDA	7.44	0.030	0.9585	7.45	16.065	7.55	0.9975	8.24

property. It can be seen that OCS as a dialdehyde derivative can significantly improve the fabric protective performance against ultraviolet irradiation. The UV protection properties of the modified fabrics are mainly attributed to the C=N, which absorbs UV efficiently (Hou et al., 2010).

K/*S* values of Direct Pink 12B dyed fabrics are shown in Tabe1. Obviously, *K*/*S* values of modified cotton fabrics were higher than that of the untreated cotton fabrics. The highest *K*/*S* values were measured in the case of cotton fabrics with OCS + EDA treatment for Direct Pink 12B. It could be explained that OCS + EDA modified cotton have more cationic groups, while direct dye possesses anionic groups ($-SO_3^-$) which can be attracted into modified cellulose surface by electrostatic (Alimohammadi et al., 2012; Hou et al., 2010; Tsatsaroni, Eleftheriadis, & Kehayoglou, 1990).

The reflective behavior of the untreated sample and cotton cross-linked with various OCS composites were investigated from wavelengths 360 to 510 nm, the results are shown in Fig. 5. It indicates that untreated and OCS, OCS + EDA modified cotton samples exhibit very similar reflectance spectra and the variations were really small in a range. However, it was evident that the OCS + APTES modified cotton had the lower reflectance values, compared to that of untreated cotton in Fig. 5. It could be attributed to the extremely low refractive index of the silica nanoparticle films and trapping of light (Hou et al., 2010).

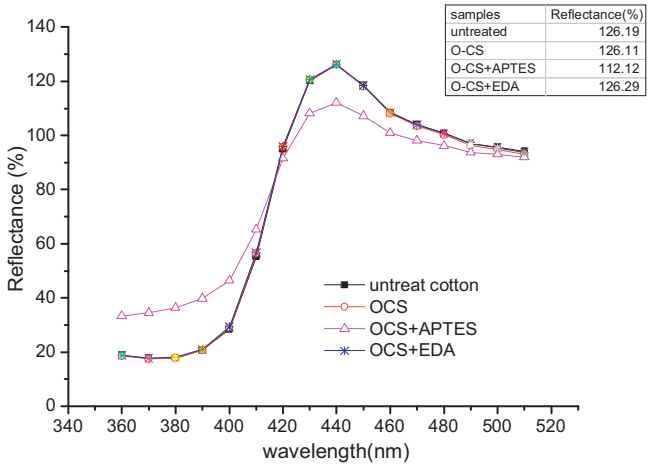


Fig. 5. Reflectance spectra of untreated and modified cotton.

3.5. Adsorption kinetics of modified cotton

Fig. 6 depicts the dyeing rate curves of untreated, OCS + EDA and OCS + APTES modified cotton at 50 °C, 70 °C and 90 °C respectively with the condition of dye concentration 2%, sodium sulfate 10 g l^{-1}, liquor ratio 1:50.

The rate of any process means the change in reactant concentration with time. Applying this definition in the dyeing process can be considered as the change in the amount of dye on fiber per unit time. Firstly Fig. 6 shows that the amount of dye on OCS + EDA and OCS + APTES modified samples is higher than that of untreated cotton respectively. Improvements in the amount of dye on modified cotton were generally attributed to heterogeneous characterize and existence of different activities sites on the surface of modified cotton with OCS. The anion of the direct dye is substantive toward cellulose and will tend to move from the external dye solution into the fiber (Ibbett et al., 2006). With the increase in temperature, the pores in the fiber enlarge, resulting in the increased surface available for the sorption, diffusion and penetration of the planar dye molecule within the pores of the fiber causing increased sorption. Besides, the diffusion of the dye in the pores is enhanced due to increased mobility of the ions at higher temperature (Chen, Lin, Wang, & Hwang, 2010; Tsatsaroni et al., 1990). However, due to the ionic attraction between pink 12B and cationized cotton was an exothermic process, the high dyeing temperature would cause hydrolytic degradation and desorption of dye from fabric to dye bath, doing harm to dyeing equilibrium of pink 12B (Bhatti, Adeel, Fazal ur, Irshad, & Abbas, 2012; Guesmi, Ladhari, & Sakli, 2013). Therefore, the untreated and modified cotton fabrics were dyed at 70 °C with Direct Pink 12B was appropriate.

To understand the applicability of the pseudo first-order and pseudo second-order for Direct Pink 12B on untreated, OSC + EDA, OSC + APTES modified cotton at different temperature, linear plots of $\log(q_e - q_t)$ versus contact time (t), t/q_t versus contact time (t) are plotted. The values of k_1, k_2, R^2 (correlation coefficient values) and the calculated q_e are shown in Table 2. The linearity of the

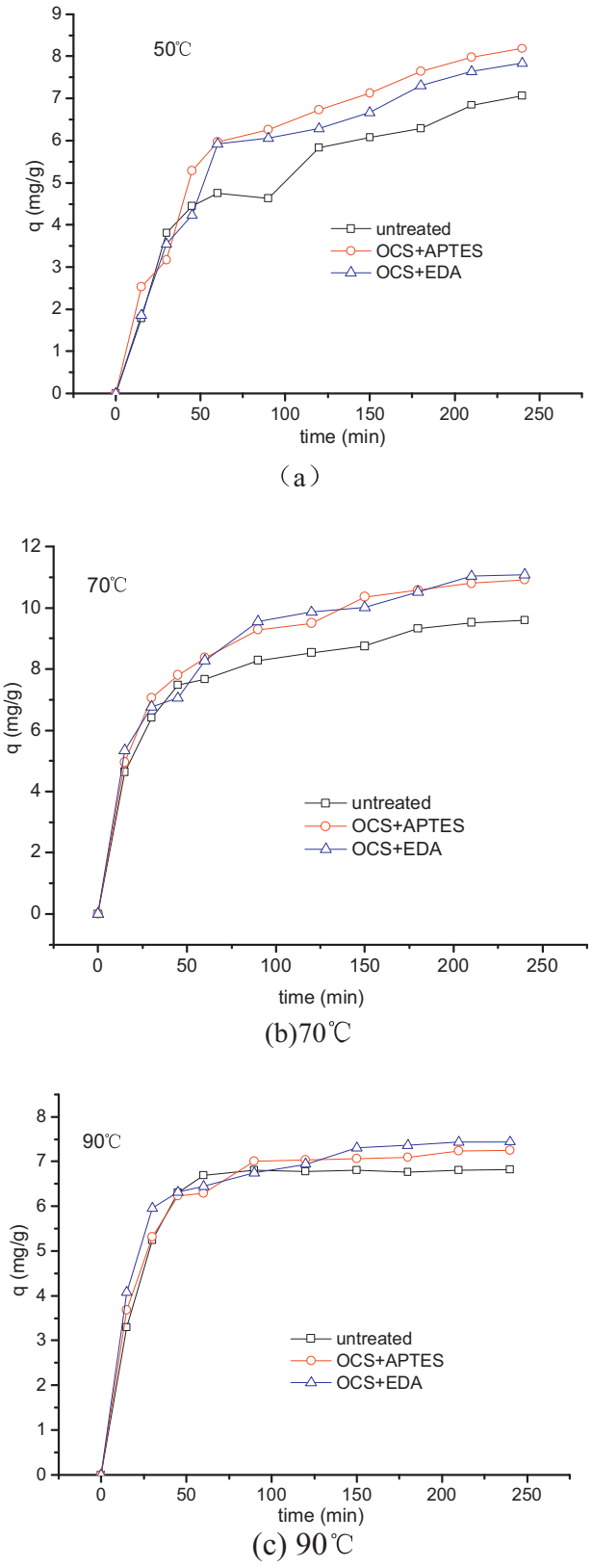


Fig. 6. Kinetics of different temperature (a) 50 °C; (b) 70 °C; (c) 90 °C (dyeing condition: dye 2%, L:R = 1:50).

plots (R^2) demonstrates that pseudo-first order does not play a significant role in the uptake of the dye (Table 2). The linear fit between the t/q_t versus contact time (t) and calculated correlation coefficients (R^2) for pseudo-second order kinetic model show that the dye up-take kinetic can be approximated as pseudo-second order kinetics (Table 2). The time of half dyeing $t_{1/2}$, which is the time required for the fabric to take up half of the amount of dye taken at equilibrium, are given in Table 2. The values of half dyeing $t_{1/2}$ for dyeing modified cotton fabrics with pink 12B dye were clearly decreased with dyeing temperature increasing, it was because high temperature can improve the diffusion rate of pigment particles through the boundary layer.

4. Conclusions

In this paper, modifications of cotton fabrics with aldehyde chitosan solution containing APTES and EDA respectively were prepared by using pad-dry-cure technique. The modified fabrics with the oxidized chitosan and different N containing agent had a significant improvement in its UV-protection and wrinkle resistant though slightly decreases in whiteness. A marked enhancement was registered in the color depth shade in modified cotton fabric dyed with Direct Pink 12B dye. Dyeing kinetic of pink 12B was found to conform to pseudo-second order kinetics. In all, multifunctional cotton fabrics with UV-protective, wrinkle resistant and good dyeing properties were achieved. So, the use of dialdehyde chitosan and nitrogen-containing reagents to modify cotton fabric is a simple, effective, eco-friendly finishing method for cotton dyeing and finishing.

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