Using Carbon Black Nanoparticles to Dye the Cationic-Modified Cotton Fabrics

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ABSTRACT: Carbon black (CB) aqueous dispersion was prepared and used to dye the cationic-modified cotton fabrics through exhaust dyeing process. The effects of CB concentration, CB nanoparticles size, dyeing bath pH, dyeing time and dyeing temperature were investigated. The color yields of dyed fabrics were evaluated on Kubelka-Munk value K/S. The surface morphologies of cationic modified and nonmodified cotton fabrics were measured by video microscope. The fabrics presented 18.9 of the color yield with the dyeing conditions: the dyeing solution contained 2% o.w.f. CB and dyeing at 80°C for 30 min with pH 13 using a 50 : 1 liquor ratio. The images of the video microscope demonstrated a clear surface profile for the cationic-modified cotton fabrics dyed with smaller CB particle size solutions. These results indicated that CB nanoparticles were suitable for dyeing the cotton fabrics. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 5194–5199, 2012

Key words: carbon black nanoparticles; K/S value; dyeing uptake; cationic-modified cotton

INTRODUCTION

Cotton is a major textile fiber for a long time and has a unique combination of properties, including high strength, durability, softness, good dyeability, biodegradability, etc.[1–3] Sulfur dyes, especially sulfur blacks are widely used to dye cotton fabrics because they have simple applied processes and considerable cheap prices.[4,5] Typically, good fastnesses of black cotton fabrics to light and wet treatments are easily obtained with sulfur dyes,[6] but during the dyeing process, various chemical agents, especially sodium sulfide, are usually used because sulfur dyes are inert and insoluble in the dye solution. During these chemical agents, the largest damage to the environment is the reducing agent sodium sulfide, which is required to reduce the particle size of sulfur dyes and dissolve dye molecule in water to enable adsorption on the fibers. Although such reducing systems are undoubtedly efficient, their irreversibility raises both economics and environmental cost for the presence of toxic sulfites and sulfides in the industrial effluent. And compared with other dyes, ideal bright color of cotton fabrics is hardly to be obtained with sulfur dyes.[7–10]

The carbon black (CB) is a strong covering power material and often widely used as inorganic pigment in the paints industry.[11,12] CB nanoparticles have many advantages, such as good absorption and refraction of light.[13] Previous researches showed that CB nanoparticles with 8-nm particle size could diffuse into polyester and acrylic fibers at the temperatures above their glass transition temperatures (T_g) in a thermal dyeing process.[14] The excellent color and fastness properties make CB nanoparticles possible application in textile dyeing field. Compared with common sulfur dye, the dyeing process of CB nanoparticles can save water and energy due to the shorter dyeing time. However, the dispersion of CB nanoparticles in aqueous solutions and adsorption of the particles to cotton fibers are critical in exhaustion dyeing process. Dyes used in exhaustion dyeing process are water soluble and have strong intermolecular interactions with the fibers. The intermolecular interactions between dyes and fibers promote adsorption to the fibers, and the particles can enter into the fibers through diffusion.[15] CB has three existing forms: primary particle, aggregates, and agglomerates. Primary particle is formed by some ceramic laminated structure. As a result of large surface area and high surface energy, primary particles fuse together in the reactor and form aggregates and agglomerates. CB nanoparticles are hydrophobic and easily aggregate in aqueous solutions.[16] An effective way of increasing hydrophilicity and dispersibility

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of the nanoparticles is introducing cationic groups, commonly quaternized amino groups, by pretreatment on the cotton fibers. This modification of cotton fibers increases the attraction between the CB nanoparticles and fibers, and enhances the dye-fibers substantivity.[17] The effects of sodium chloride and pH on CB dyeing properties for cotton, nylon, and wool fabrics have been presented. However, CB nanoparticles used to cationic surface modified cotton fabrics has not reported in the previous research.

The aim of this work is to investigate the main dyeing factors of CB nanoparticles to cotton fabrics modified with cationic modifier. Dyeing properties such as the *K/S* value, dye uptake are measured and analyzed. The DZ3-video focus-exchanged microscope images are also used to show the morphology of the CB nanoparticles dyed on cationic-modified cotton fabrics surface.

EXPERIMENTAL

Materials and chemicals

The knitted cotton fabric (weight 141.0 $g.m^{-2}$) produced by Jiangsu Hongdou Industrial (Wuxi/China) was desized and scoured. Sodium hydroxide was obtained from Sinopharm Chemical Reagent, China. Dispersing agent NNO (sodium salt of polynaphthalene sulphonic acid) was supplied by Zhejiang Runtu, China. Cationic modifier and CB were prepared by Key Laboratory of Eco-Textile, Ministry of Education, Jiangnan University.

Methods

Preparation of CB aqueous dispersion system

CB and dispersing agent NNO (mass ratio 2 : 1) were added into water. After stirring, the mixture was grinded by ultrasonic at 800 W for 30 min.

Modified cotton fabrics with cationic modifier

The cotton fabrics were modified with 2% o.w.f. cationic modifier in the aqueous solution (liquor ratio 30 : 1) at 20°C for 50 min with dyeing bath pH 13. Cotton fabric, which surface carrying negative charge, would be adsorbed the cationic modifier due to the electrostatic attraction. This makes the cotton fabric surface with a certain amount of positive charge.

Dyeing process

The dyeing process for the CB was shown in Figure 1. CB and dispersing agent NNO were mixed with the ratio of 2 : 1, and the bath ratio was 50 : 1. Dispersant NNO, which hydrophobic groups pointed to dye particles and hydrophilic groups pointed to the surrounding water system, was adsorbed to the dye particles surface and formed micelle structure. The negative micelle would attract the anti-ions and generated electrical double-layer structure. Because of the presence of electrical double-layer, CB nanoparticles would be separated stably by the electrostatic repulsion. Cationic-modified cotton fabrics were dyed at different conditions. The fabrics was washed, soaped, and finally, rinsed in cold water.

Measurement of Zeta potential and particle size

The Zeta potential and particle size of the diluted CB aqueous dispersion system were measured by a Malven Mastersiser Nano-ZS90 particle size analyzer (Malvern, UK) at 25°C.

Measurement of dyeing exhaustion

The dyeing exhaustion (%, *E*) was determined via spectrophotometer. The absorbance of the dissolved dye samples before and after dyeing was measured with 2100 UV/Visible Raster Spectrophotometer, at the wavelength $\lambda = 540$ nm.[18] The percentage of dyeing bath exhaustion (%, E) was calculated according to equation,

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

where A_0 and A_1 are the absorbance of the dyeing bath before and after dyeing, respectively.[19]

Measurement of color

The color properties of the samples were determined with an Xrite-8400 spectrophotometer obtained from America X-Rite under the illuminant D65 using the 10° standard observer.[20] The relative color yield and staining on white ground were determined with the Kubelka-Munk equations. The color yield was investigated by the K/S value,

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

where *K* was the absorption coefficient, *S* was the scattering coefficient and *R* was the fractional reflectance (value from 0 to 1) of the dyed substrate at the wavelength of minimum reflectance. The *K/S* values were proportional to the dyeing color.[21]

Video microscope observations

The fabrics were photographed under a 4900 magnification with a DZ3-Ultra High Magnification Zoom Microscope supplied by Union Optical, Japan.

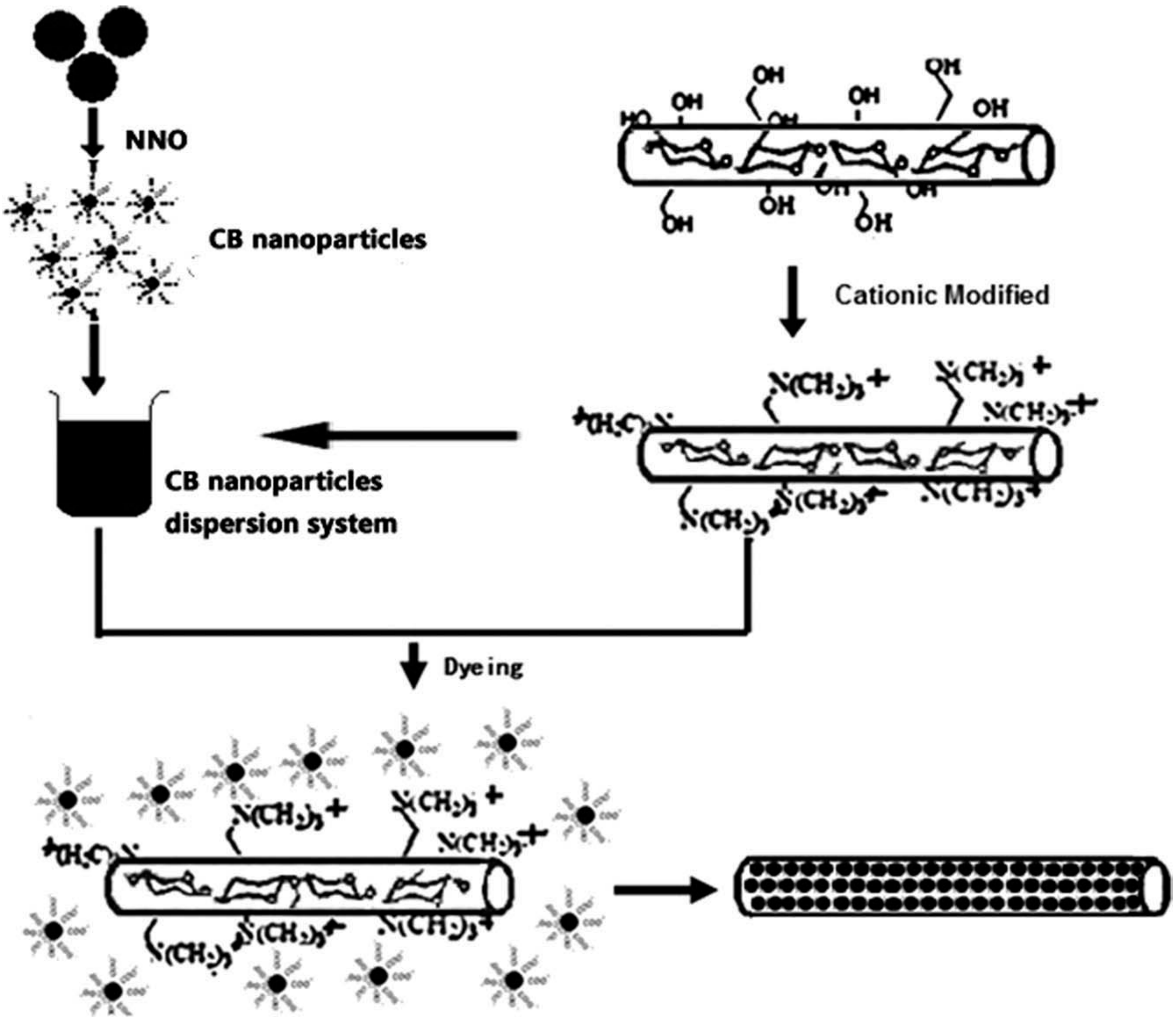


Figure 1 Dyeing process for CB.

RESULTS AND DISCUSSION

The effects of concentrations of CB

To investigate dyeing behaviors of CB, the effect of concentrations on the *K/S* and dyeing uptake was discussed. From Figure 2, it could be seen that the dyeing uptake significantly decreased with the increase in the concentration of CB, from 99.2 to 19.9%. It was suggested that the absorptions of CB were up to a saturation value, and with the increase of the CB concentration A_0, (A_0–A_1) almost unchanged, which resulted in the decrease of dyeing exhaustion.

Figure 2 showed that the *K/S* value of the fabrics increased when the amount of CB increased, and the *K/S* values (before and after soaping) reached the maximums, 18.8% and 14.6% at the concentration of CB 2% o.w.f., respectively. After that the *K/S* value had a little decrease with the increasing amount of

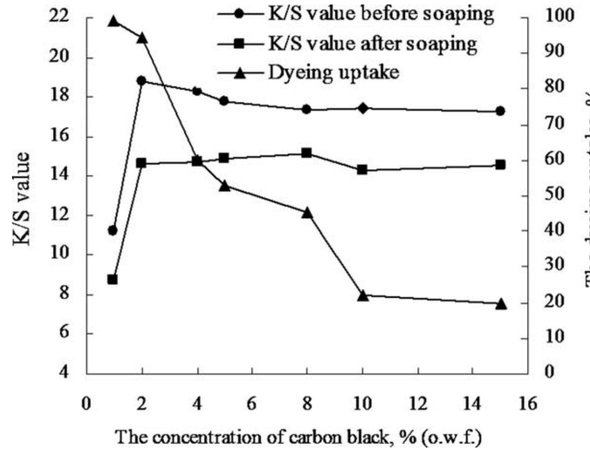


Figure 2 The effects of different CB concentrations on K/S value and dyeing uptake of modified cotton.

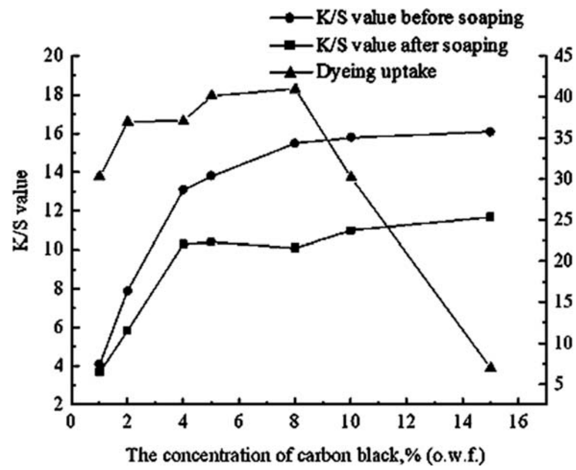


Figure 3 The effects of different CB concentrations on K/S value and dyeing uptake of unmodified cotton.

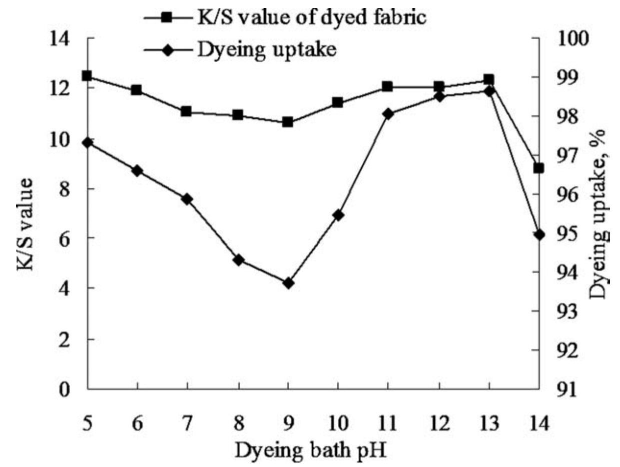


Figure 4 The effects of pH on the K/S and dyeing uptake.

CB, the particle size didn't increase and maintained approximate 125nm by Malven Mastersiser Nano-ZS90 particle size analyzer. The reason for the phenomenon was probably that the absorption of CB on cotton fabrics was also up to a saturation value. Comparing the two curves (before and after soaping), the *K/S* value of the former is 32% bigger than that of the latter. It might be attributed to the relatively poor bonding force between the fabrics and dyes, resulting in CB nanoparticles to fall off from the surface of cotton fabrics. Compared with the modified cotton (Fig. 3), the maximum *K/S* values (before and after soaping) of the unmodified cotton were 16.1 and 11.7 at the concentration of CB 15% o.w.f., respectively. The maximum dyeing uptake was only 41%, and dyeing exhaustion value was too lower to satisfy the industrial requirements.

The effects of dyeing bath pH

The modified cotton fabrics were dyed with the dyeing baths (CB, 1% o.w.f.) with different pH values at 80°C for 30min.The dyeing uptake and *K/S* values were shown in Figure 4. It could be seen that the *K/S* values and dyeing uptakes were decreased with increased pH value from 5 to 9. The *K/S* value and dyeing uptake reached the minimum values at pH 9, respectively. When the pH value of dyeing bath was raised continuously, the dyeing uptake and *K/S* value were increased correspondingly. At pH = 13, *K/S* value and dyeing uptake were 12.3 and 98.6%, respectively, and reached the maximums. But after that the dyeing uptake and *K/S* value rapidly reduced.

The mainly reasons for the complicated variation trend were possible that the pH value of dyeing bath had effects on not only the surface protonation and the expansion of cotton fabrics but also on the Zeta potential and particle size of CB. When the pH value of dyeing bath was 5, cotton fabrics were easily hydrolyzed, which lead to the degradation of cellulose molecular chain. At this condition, the amorphous region and grooves of the cotton fiber enlarged. The quaternary ammonium of cationic cotton fabric surface was protonated and CB nanoparticles with much negative charge on the surface could be adsorbed onto the modified cotton fabrics via ion-ion linkages. The electrostatic attractions between dyes and fibers and availability of nucleophilic amino groups were maximized. With the pH value of dyeing bath increasing from 5 to 9, it aroused the less changes of the cotton fabrics structure and lower protonation of quaternary ammonium salt which made less affinity between cotton fabric and CB, leading to the *K/S* value and the dyeing uptake decreasing. With the increased pH values, the dyes were absorbed to cotton fibers easily due to the inflated cotton fiber in the solution and expansion of the distance in the fibers. Moreover, from the Figure 5, it was obviously shown that CB surfaces became more negative due to the ionization

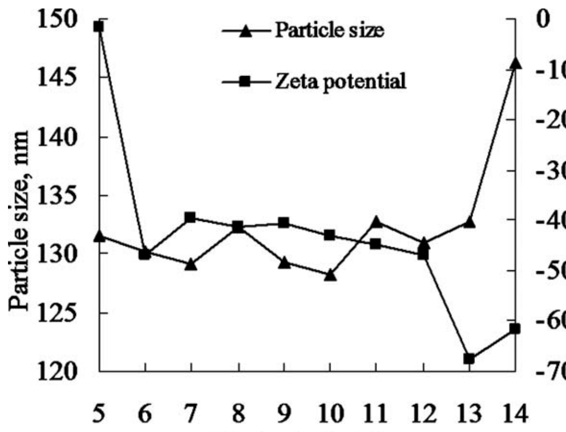


Figure 5 The effects of pH on the particle size and Zeta potential.

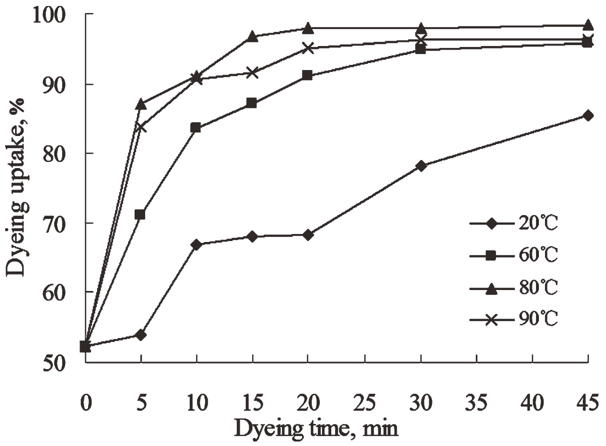


Figure 6 The effects of dyeing time and temperature.

of sulfonic sodium with the increase of dispersing agent NNO. The *K/S* value and dyeing uptake became larger and up to the largest at pH 13, but the double-layer structure of CB surface was compressed for vast quantities of sodium ion in the dye solution were adsorbed on the CB surface, leading to the absolute value of Zeta potential and electrostatic attraction decrease. With the increase of the dye solution pH value, the electrostatic repulsion among CB nanoparticles decreased, which could lead to aggregate in the CB nanoparticles. When the size of CB nanoparticles enlarged, the resistance to enter the fibers grooves of the CB increased.[22]

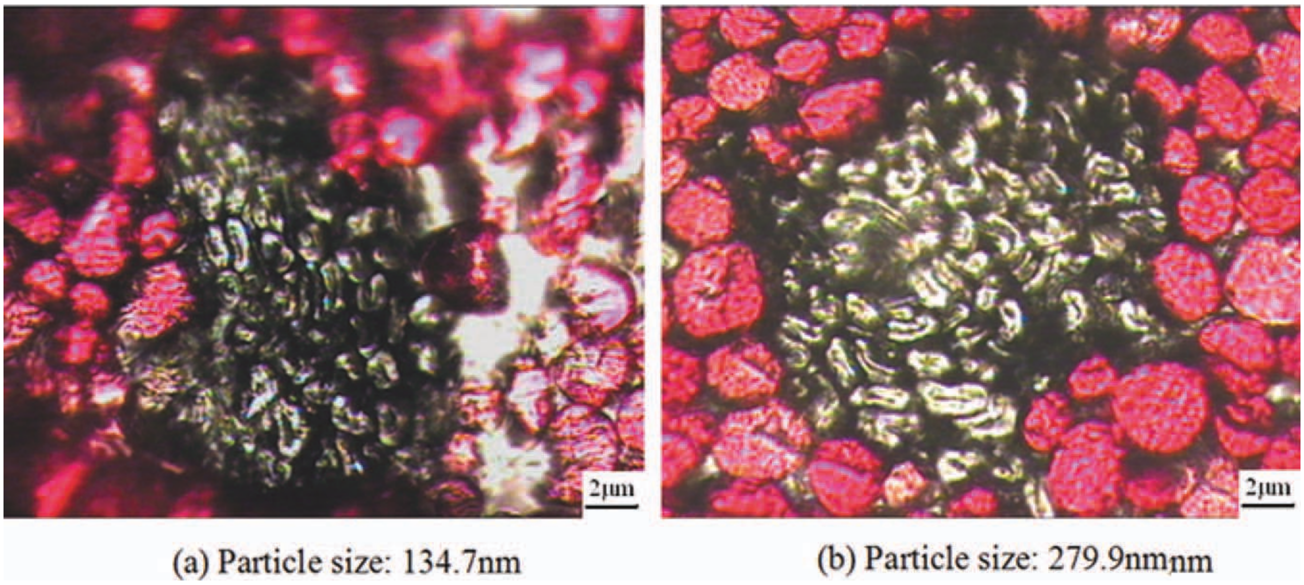
The effects of dyeing time and temperature

The effects of dyeing time and temperature on the dyeability with CB were investigated. The dyeing processes were implemented at different temperatures and times and the results were shown in Figure 6.

From Figure 6, only a few dyes were fixed onto cotton fabrics at a low temperature. When the temperature was changed from 20 to 80°C, the fixed CB dyes was increased around 35%. After the temperature was up to 90°C, the fixed dyes were decreased. These observations could be explained that the swelling fibers at high temperature could enhance the dye diffusion. With the molecular thermodynamics movement increasing, much more CB nanoparticles were absorbed onto the fabrics, and the CB nanoparticles would fall off from fiber surface at a higher temperature. The dyeing time had an obvious effect on the dyeing uptake at the beginning of 30 min, but the changes were not remarkable any longer after 30 min. It could be explained that the dyes entered the fabrics continuously until the absorption was saturated. Compared with the dyeing uptake at different temperatures for 30 min, the modified cotton fabrics dyed at 80°C had an acceptable dyeing effect.

The distribution of CB nanoparticles on cotton fibers

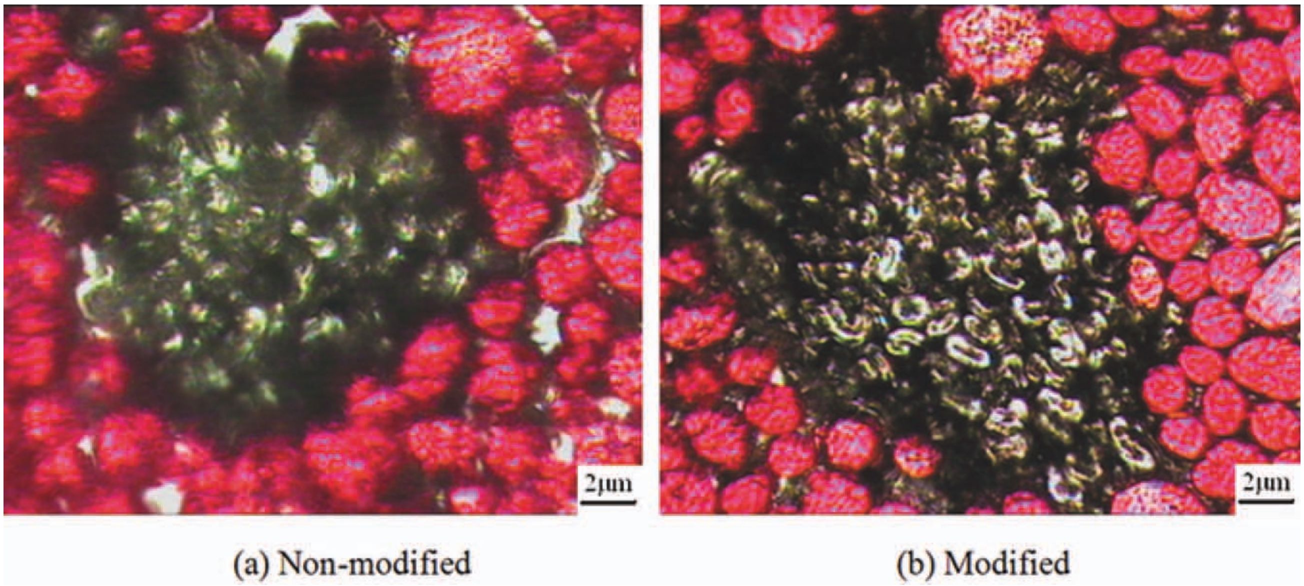
The images of the video microscope of the cotton fabrics were shown in Figure 7. The kidney-shaped cross section of cationic-modified cotton fibers dyed with different sizes of CB nanoparticles were colorless region, and CB nanoparticles were only distributed in the cotton fiber grooves, just as "ring-dyeing." The CB nanoparticles with small sizes were easier to penetrate into the cotton fibers grooves, while the larger ones mainly only entered the yarn surface.[23]



(a) Particle size: 134.7nm

(b) Particle size: 279.9nmnm

Figure 7 The cross section diagrams of dyed cationic-modified cotton fabric with different particle size CB (CB 5% o.w.f.; TX-10 : CB = 1 : 5; pH = 7; bath ratio 30 : 1; 80°C, 30 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



(a) Non-modified (b) Modified

Figure 8 The cross section diagrams of dyed cotton fabric with or without cationic modified (CB 1% o.w.f.; NNO : CB = 1 : 2; pH = 13; bath ratio 30 : 1; 80°C, 30 min, particle size: 127.3 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It showed that the surface profile of modified cotton fabrics dyed with CB was relatively clearer [Fig. 8 (b)] than the one without modification [Fig. 8 (a)]. The results indicated that less CB nanoparticles were absorbed on the nonmodified cotton fibers surface for the weak affinity.[24,25] The color of the fiber was light, so the outline edge was indistinct visually.

CONCLUSIONS

The CB aqueous dispersion system was prepared by adding NNO as dispersing agent, and cationic-modified cotton fabrics were dyed with this CB aqueous dispersion system in different dyeing conditions. The feasible dyeing process was concluded as follow: CB concentration 2% o.w.f.; dyeing temperature 80°C; dyeing time 30 min; liquor ratio 50 : 1; pH value of dyeing bath 13. The kidney-shaped cross section of cationic-modified cotton fibers dyed with different sizes of CB nanoparticles were colorless region, and CB nanoparticles were only in the cotton fiber grooves, just as “ring-dyeing.” After cationic modification, the cotton fiber could have a dark color for the adsorbability of the anionic CB.

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