Available online at www.sciencedirect.com
SCIENCE DIRECT®

Dyes and Pigments 72 (2007) 144–149

DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Coloration of textiles with self-dispersible carbon black nanoparticles

Dapeng Li[1], Gang Sun*

Division of Textiles and Clothing, University of California, Davis, CA 95616, USA

Received 8 June 2005; received in revised form 2 August 2005; accepted 18 August 2005
Available online 5 October 2005

Abstract

Cotton, wool, acrylic and nylon fabrics can be directly dyed by using surface modified carbon black (CB), self-dispersible carbon black (SDCB), nanoparticles through an exhaustion process. The SDCB nanoparticles were prepared by refluxing CB particles in nitric acid for certain time to result in hydrophilic carboxylic groups on their surfaces. The SDCB nanoparticles behaved similarly to direct or acid dyes in dyeing cotton, acrylic and nylon fibers. The SDCB nanoparticles were characterized by infrared spectroscopy and particle size analyzer. The SDCB-dyed fabrics showed good colorfastness against crocking. However, the wash fastness of the nanoparticle-dyed cotton fabrics is relatively lower than the crocking fastness due to the hydrophilic feature of the SDCB nanoparticles. Direct employment of the nanoparticles in dyeing opens new applications of nanotechnologies in textile production.

Keywords: Nanoparticles; Carbon black; Pigments; Exhaustion dyeing

1. Introduction

The development of nanotechnologies has stimulated research on applications of nanosized pigment particles in textile processing [1]. One possible application is to directly employ pigment nanoparticles in textile dyeing. Such an approach could be achieved if the nanoparticles can be reduced to a small enough size and the particles can be dispersed well to avoid aggregation of the nanoparticles in dye baths. Previous research has shown that surfactant dispersed CB nanoparticles in nominal size of 8 nm were able to diffuse slowly into polyester and acrylic fibers at temperatures above their glass transition temperatures (Tg) in a thermal dyeing process [2]. However, in exhaustion dyeing of cotton, wool, acrylic and nylon fabrics, dispersion of CB nanoparticles in aqueous solutions and adsorption of the particles onto surface of the fibers are critical. Traditional dyes employed in exhaustion dyeing of the fibers are water soluble and have strong intermolecular interactions with the fibers. The intermolecular interactions between dyes and surfaces of fibers serve as a driving force for the adsorption, and the particles can enter into the fibers through diffusion consequently [3]. CB nanoparticles are hydrophobic in nature and tend to aggregate in aqueous solutions. Thus, increasing hydrophilicity and dispersibility of the nanoparticles is the key to the nanoparticle dyeing of fabrics through exhaustion process.

In recent years, single-walled carbon nanotubes (SWNTs) have been studied for many applications due to its outstanding electric, mechanic and thermal properties, as well as the flexibility of being functionalized for various applications [4–7]. Among those functionalization methods, nitric acid oxidation was proven to be a simple and effective way of generating carboxylic groups at the ends of SWNTs [8,9]. Because of the similarity between CB nanoparticles and SWNTs in terms of the graphite layer structures [10], the same method was employed to modify surfaces of CB nanoparticles. Thus, the oxidative treatment should be able to generate carboxylic groups on the surfaces of the CB nanoparticles, so as to make the modified nanoparticles self-dispersible in water and adsorptive to fibers that contain functional groups ready

---

* Corresponding author. Tel.: +1 530 752 0840; fax: +1 530 752 7584.
E-mail addresses: dl325@cornell.edu (D. Li), gysun@ucdavis.edu (G. Sun).

[1] Current address: Department of Textiles and Apparel, Cornell University, Cornell, NY, USA.

0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.08.011

to interact with carboxylic groups. If both can be achieved, an exhaustion dyeing of cellulose, wool, acrylic and nylon fabrics using the modified CB nanoparticles without additional dispersing agents would be possible, provided that the size of nanoparticles is small enough to diffuse into fibers properly.

2. Experimental

2.1. Materials

Carbon black nanoparticles, 8 nm in size, were supplied by Columbian Chemicals Co. (Akron, OH), and nitric acid (70%) was purchased from EMD Chemicals Inc. (Gibbstown, NJ). Both were used without any further treatment. Cotton (#400, bleached and desized), wool (unbleached worsted wool, #527), acrylic (#867 and #974), and nylon (#306A, filament 6.6, Taffeta) fabrics were purchased from TestFabrics Inc. (West Pittston, PA) and used after scouring and conditioning.

2.2. Preparation of SDCB nanoparticles

CB nanoparticle powders (8 g) were mixed with 600 mL of 70% nitric acid in a 1000 mL flask, and the mixture was refluxed at a given temperature for a certain period of time. The mixture was then poured into 12 50-mL plastic centrifuge tubes, with approximately 40 mL in each tube and capped. The tubes containing the mixture were then centrifuged at 2500–3000 rpm in a Damon/IEC Division HN-SII centrifuge (Muskegon, MI) for 30 min. The supernatant was then decanted and 25 mL of distilled water was added to each tube. The tubes were shaken well to re-disperse the sediment and centrifuged for another 15 min to separate the nanoparticle powders from the dispersion. The separated powders were then placed in an oven and dried at 80 °C overnight for dyeing and further analyses.

2.3. Dyeing of fabric

Fabrics are dyed following an exhaustion procedure with a liquor ratio of 50:1, or as otherwise specified. The dye baths contained varied concentrations (on-weight-fabric, owf) of SDCB nanoparticles with different pH values. The dyeing was carried out at a temperature of 100 °C for 30 min. The fabric was cut into 10 × 10 cm swatch (1.2 g) and then soaked into a dye bath. Sodium chloride was added as an electrolyte to assist exhaustion of the SDCB particles. The mixture was heated to the dyeing temperature for 30 min, and the fabric was then rinsed in both tap water and deionized water. After being placed in a conditioning room (21 °C and 65% relative humidity) for over 24 h, the dyed fabrics were weighed for measuring particle uptakes by the fabrics and stored for analyses.

2.4. Instrumental analysis

The nitric acid treated CB nanoparticles were ground for 5 min and then further heated at 130 °C for 60 min in a Lindberg/Blue Mini-Mite tube furnace (Kendro Laboratory Products, Inc., Asheville, NC) to drive off nitrogen oxide, a side product of the oxidation. A Nicolet Magna-IR 560 spectrometer (Nicolet Instrument Corp., Madison, WI) was used to measure Fourier Transform Infrared (FTIR) spectra of the particles. Diffused CB nanoparticles in fibers were characterized by a transmission electron microscope (TEM), Philips EM400 with Goniometer (FEI Company, Hillsboro, OR). A Color-Eye® 7000A Spectrophotometer (GretagMacbeth™, New Windersor, NY) was used to measure the *K/S* value of the dyed fabrics. An LB-500 DLS Particle Size Analyzer (Horiba Instruments Inc., Irvine, CA) was used to measure the size distribution of the CB nanoparticles.

Content of carboxylic groups on the treated nanoparticles was measured by using a titration method. Treated or untreated CB particles (0.010 g) were dispersed in 50 mL of distilled water for 5 min, and the mixture was titrated by a standard 0.01 N sodium hydroxide solution. Three replicates were conducted for each sample. The difference of titrate volumes of untreated and treated CB particles was employed to calculate mMol of carboxylic group per gram of SDCB.

3. Results and discussion

3.1. Preparation and characterization of SDCB nanoparticles

CB nanoparticles are hydrophobic and stay in aggregated form in aqueous environments, which makes it difficult to be adsorbed onto surfaces of and then diffused into most textile fibers, particularly the hydrophilic ones. Oxidative treatment of CB nanoparticles is effective to increase the hydrophilicity due to the generation of carboxylic groups on particles' surface. Nitric acid, an oxidizing agent, can attack some imperfect areas of the CB nanoparticles during refluxing, which leads to the formation of carboxylic acid groups (–COOH) on the surfaces of CB nanoparticles, similar to the oxidation of SWNTs [8,9]. Longer reaction time produces more carboxylic groups on the particles, which can be observed from infrared spectra of the nanoparticles (Fig. 1), and potentially reduces particle sizes. Comparing FTIR spectra of the CB nanoparticles that were treated in 70% nitric acid for different durations (Fig. 1), we can find that –COOH ($\sim 1720\ \mathrm{cm^{-1}}$) appeared on all samples, and the intensities of the bands increased as the refluxing time was prolonged. Analysis of the intensity of $1720\ \mathrm{cm^{-1}}$ band versus reflux time indicates that 2 h of refluxing yields maximum amount of –COOH groups on the SDCB nanoparticles. From Fig. 1, we can also find other major features of the SDCB nanoparticles, including –OH at $\sim 3400\ \mathrm{cm^{-1}}$, C=C at $1600\ \mathrm{cm^{-1}}$, N=O at $1384\ \mathrm{cm^{-1}}$, and C–O at $\sim 1210\ \mathrm{cm^{-1}}$. The occurrence of the strong peak of N=O is presumably contributed to the unreacted nitric acid and various forms of nitrogen oxides being reduced from nitric acid [11]. These impurities are physically trapped inside or adsorbed on the nanoparticles during the centrifugation process.

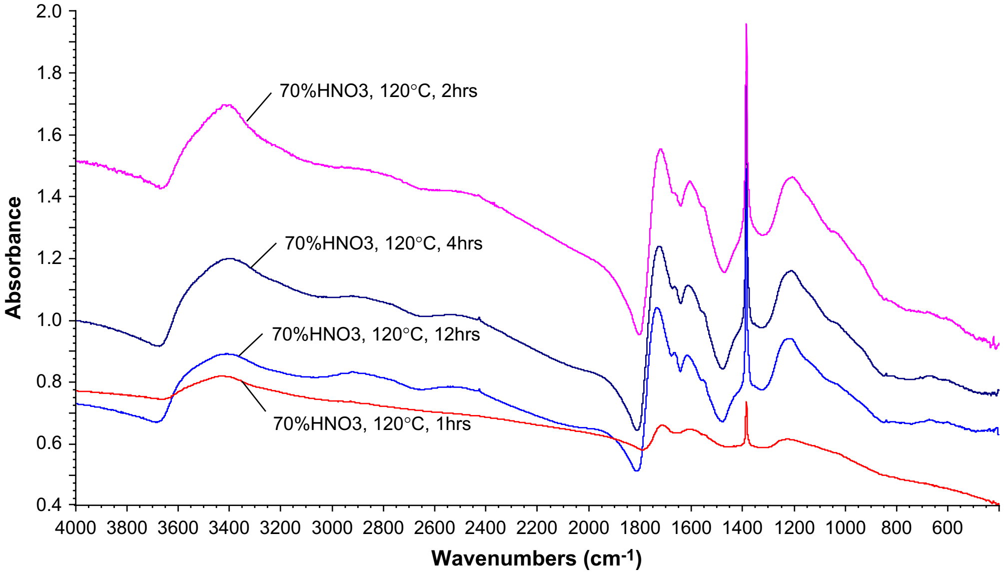

Fig. 1. FTIR spectra of CB nanoparticles after nitric acid oxidation treatment for varied durations. The size of CB nanoparticles = 8 nm.

The physically trapped nitrogen oxides could be detrimental in textile applications since in water they will become nitrous acid. In order to remove any residual nitrogen oxides the SDCB nanoparticles were further heated at 130 °C before being applied to dyeing. FTIR spectra of the nanoparticles before and after 130 °C treatments indicate that the removal of nitrogen oxides trapped in nanoparticles was possible, which can be viewed at the disappearance of absorbance band of 1384 cm^{-1} (Fig. 2). Carboxylic carbonyl band, on the other hand, did not change significantly, with the intensity of 1720 cm^{-1} band lost about 12%. These results suggest that the heat treatment of SDCB nanoparticles can effectively remove the undesired impurities without causing significant decarboxylation. A traditional titration using standard sodium hydroxide solution revealed a content of 6.6 mMol per gram of the carboxylic groups existing on the final SDCB nanoparticles.

The carboxylic groups could be produced at most defect areas of the CB nanoparticles by the oxidation reaction, and as a result the reaction could further reduce the nanoparticle size. Fig. 3 shows a plot of particle size distributions measured by an LB-500 Particle Size Analyzer. The nominal size of the CB nanoparticles was 8 nm, and a surfactant assisted dispersion showed a particle distribution of 10–80 nm with an average size above 40 nm, indicating low level of aggregations of the nanoparticles. The particle size distribution of SDCB without using surfactants was still in the range of 10–80 nm, but a little broader. This result may be due to the surface oxidation of the particles and addition of the carboxylic acid groups. Although a similar level of aggregation of the SDCB

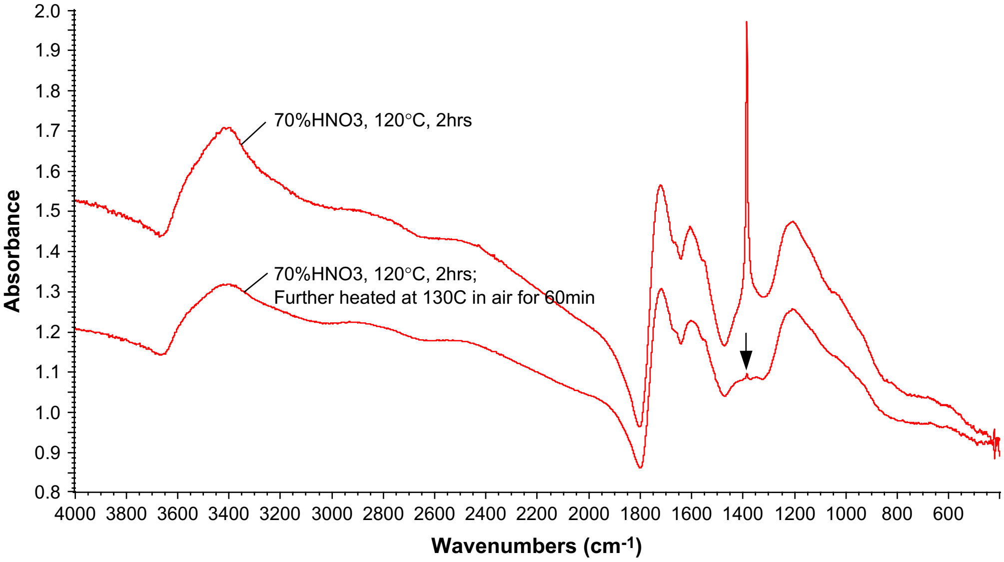

Fig. 2. FTIR spectra of CB nanoparticles before and after further heat treatment.

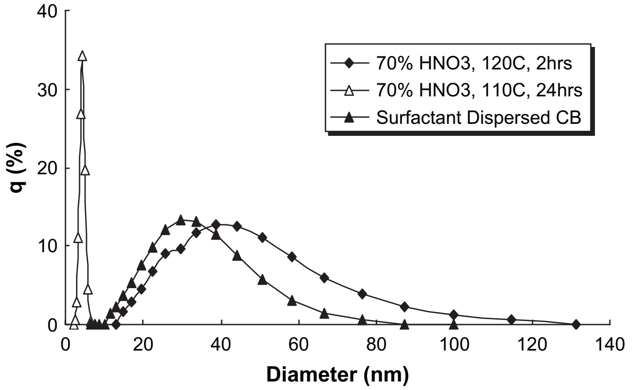

Fig. 3. Dynamic light scattering size distribution of the CB nanoparticles in aqueous dispersions at pH 12.

nanoparticles still exists, the nanoparticles are self-dispersible without assistance of surfactants. An overnight acid oxidation treatment of the CB nanoparticles caused dramatic reduction of the particle size, possibly due to oxidative degradation of the CB nanoparticles and repulsion among the oxidized particles (Fig. 3). Accompanying a dramatic decrease in size, however, the yield of oxidized nanoparticle powders was also decreased compared with those treated with 70% nitric acid at 120 °C for 2 h. When the nanoparticles are further oxidized the fragmented products may contain more carboxylic acid groups and become soluble in aqueous solution, which contributes to the low yield of treated CB nanoparticles.

3.2. Dyeing of cotton fabrics with SDCB nanoparticles

The carboxylic groups on SDCB nanoparticles significantly increase hydrophilicity of the particles and make them self-dispersible in water. Such a change on the surface of the nanoparticles is equivalent to adding anionic groups to disperse dyes. Thus, once dispersed in aqueous dye bath, the SDCB nanoparticles become interactive with cellulosic fibers through hydrogen bonding and dipole–dipole interaction, and are potentially applicable to fibers that can be colored by anionic dyes. To prove this hypothesis, the SDCB nanoparticles were employed in dyeing of cellulosic fabrics following a direct dyeing process. Fig. 4 shows *K*/*S* values of the nanoparticle-dyed cotton fabrics. Similar to direct dyeing of cotton fabrics, both alkaline condition and addition of NaCl showed remarkable effects on the coloration of the fabrics. Higher pH in the dye bath, particularly above 10, enhances uptake of the nanoparticles on fabrics because the alkaline condition further solubilizes the nanoparticles and swells cotton fibers. The addition of NaCl increased exhaustion of the particles and consequently the *K*/*S* value of the dyed fabric due to an electrolyte effect. However, the exhaustion rates of SDCB on cotton fabrics were very low ($<10\%$), presumably due to the fact that only a small portion of the nanoparticles is dispersed into the desired nominal size, i.e. 8 nm, while most of the particles remain aggregated (Fig. 3). With the observed low exhaustion rate, it is reasonable to believe that only the well-dispersed 8 nm SDCB nanoparticles are able to adsorb and diffuse into fibers during the dyeing process and the aggregates with much larger sizes stay in the dye bath without being exhausted.

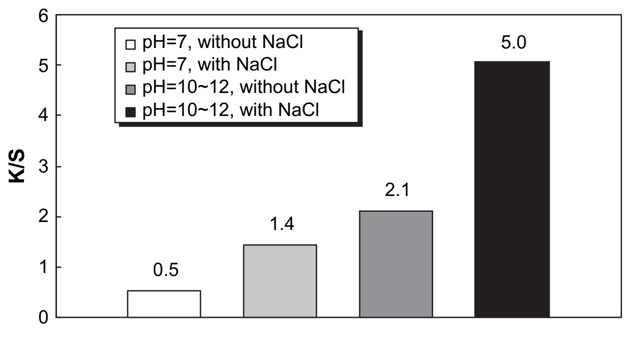

Fig. 4. Effect of pH and salt (nanoparticle concentration = 5% owf; liquor ratio = 100:1).

Addition of sodium chloride, an electrolyte, to dye bath is a common strategy used in direct dyeing of cellulose through an exhaustion procedure. It is generally believed that the electrolyte can shield the negative surface charges on cellulose in dye bath and accelerate the adsorption and diffusion of anionic direct dye molecules in the fibers [12,13]. Because the carboxylic (–COOH) groups on SDCB nanoparticles can be completely converted to carboxylate groups ($-COO^-$) under alkaline condition, the nanoparticles could interact with cellulose directly. In addition, alkaline dye solution swells cellulose and therefore makes the fibers more accessible to the diffusion of the adsorbed SDCB nanoparticles from the surfaces towards the center of fibers.

Fig. 5 shows the *K*/*S* measurements of cotton fabrics dyed at higher concentrations of the nanoparticles as well as those after further treatments including washing and hydrogen peroxide bleaching. Apparently, increasing the nanoparticle concentration in dye baths leads to increased *K*/*S* values. A minimum SDCB concentration of 25% owf was needed to achieve a saturated *K*/*S* value on the fabric. Since the SDCB exhaustion rate was very low (less than 10%) more concentrated dispersions could provide sufficient non-aggregated nanoparticles to diffuse into the fibers. Thus, to increase

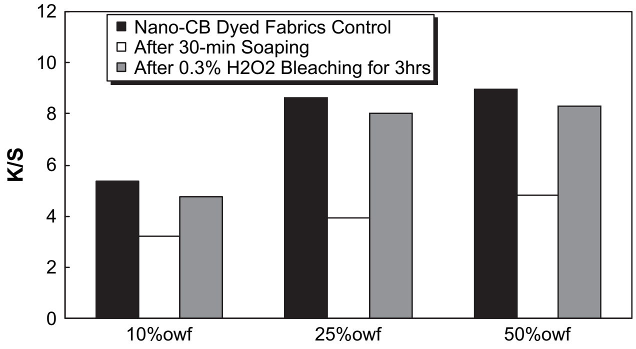

Fig. 5. Effect of washing and H_2O_2 bleaching (pH = 12; detergent concentration = 0.15% and washing temperature = 100 °C; bleach temperature = 40 °C).

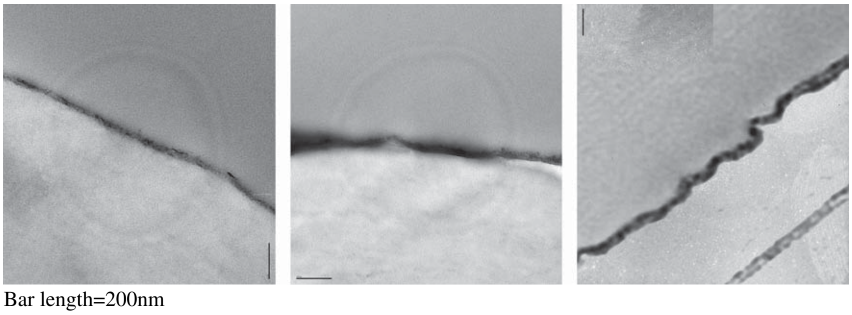

Fig. 6. TEM images of self-dispersible CB-dyed cotton fabrics (lighter sections are cotton fibers). (a) 10% owf, (b) 25% owf and (c) 50% owf; pH = 12.

exhaustion rate and improve dyeing efficiency, smaller and better dispersed CB nanoparticles are required.

On the other hand, the SDCB-dyed fabrics are vulnerable to washing, and an approximate 50% decrease of *K*/*S* has been observed for all the samples after washing. Smaller SDCB nanoparticles can easily diffuse into the fibers and can then easily diffuse out when subject to washing. A fixation step, similar to fixation of direct dyes, might be necessary to improve wash fastness of the nanoparticles in fabrics. H_2O_2 bleaching was unable to affect the color as seriously as the washing, and each bleached fabric basically holds the same *K*/*S* value as those non-bleached.

Transmission electron microscopic (TEM) images of the nanoparticle-dyed fibers, as shown in Fig. 6, indicate that a nanoparticle layer formed on the surfaces of the cotton fibers. The SDCB nanoparticles should have penetrated into cellulose but stay mostly on the internal side of the surface since the dyed fabrics possess very good crocking fastness but low wash fastness of the color (Fig. 7). However, both the coverage of fiber's surface and the uniformity of the layer are improved with the increase of the SDCB concentration. The fabric dyed at 50% owf shows the most uniform layer surrounding the fibers with an approximately 100 nm thickness.

3.3. Dyeing of other fabrics with SDCB nanoparticles

Because of the anionic and self-dispersible characteristics, the SDCB nanoparticles can directly interact with all polymers that contain cationic groups such as acid dyeable acrylic, wool and nylon under proper pH ranges. Thus, acid dyeable acrylics, wool and nylon fabrics were directly tested in the nanoparticle dyeing as examples. Fig. 8 shows the *K*/*S* value difference between two types of acrylic fibers dyed with the SDCB nanoparticles. Obviously, only acid dyeable acrylics can exhaust the nanoparticles remarkably while the cationic dyeable acrylics could not, which agrees very well with the ionic feature of the carboxylate groups on the CB nanoparticles.

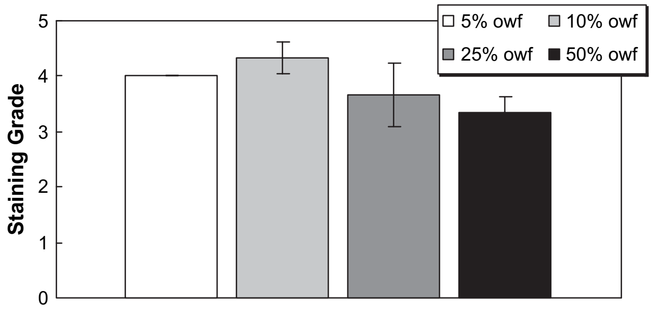

Fig. 7. Dry crocking test of the CB nanoparticle-dyed cotton fabrics.

Fig. 9 shows *K*/*S* measurements of nylon and wool fabrics dyed by the SDCB nanoparticles. As we have expected, under low pH, more and more amino groups of protein and polyamide are being protonated and therefore interact with the anionic nanoparticles more significantly, resulting in increased *K*/*S* values. Apparently, wool fabrics demonstrated higher exhaustion of SDCB, which could be caused by higher surface areas in wool fibers than in nylon fibers. In addition, nylon fibers have higher crystalline and lower swelling ability in water compared to wool [14], which could be other important contributors to lower exhaustion rate. Both Figs. 8 and 9 further demonstrated the feasibility of using the specially prepared nanoparticles in direct dyeing applications.

4. Conclusions

SDCB nanoparticles have been prepared through an oxidative treatment. FTIR analysis confirmed that the resulting

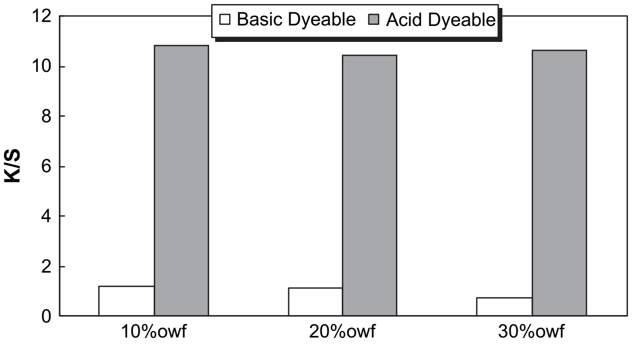

Fig. 8. *K*/*S* measurement of cationic dyeable and acid dyeable acrylic fabrics dyed by the nanoparticles. pH = 1.5.

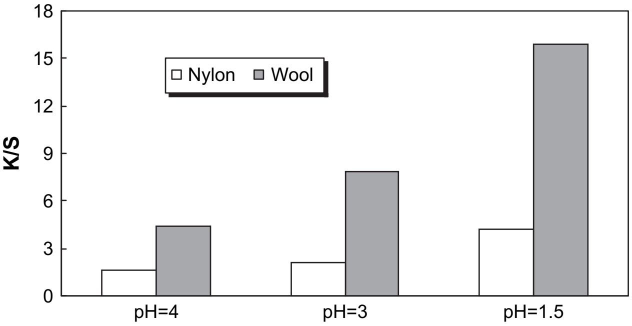

Fig. 9. *K*/*S* values of nylon and wool fabrics dyed by the CB nanoparticles. Nanoparticle concentration = 30% owf; NaCl concentration = 10% owf; liquor ratio = 40:1.

nanoparticles contain certain amount of carboxylic groups and the amount of the carboxylic groups increased as oxidation time prolonged. The SDCB nanoparticles can be applied in coloration of some natural and synthetic fibers through an exhaustion process without addition of dispersing agents and binders. The exhaustion rate of the nanoparticles by the fabrics is very low due to the fact that only a small portion of the nanoparticles is dispersed in singular particle form. The SDCB nanoparticle-dyed cotton fabrics were relatively vulnerable to washing due to soluble features of the treated nanoparticles. The color crocking fastness of the dyed fabrics was much better than wash fastness, indicating the penetration of the nanoparticles into fibers.

Acknowledgements

The authors acknowledge financial supports of this project from Jastro-Shields Scholarship Award from University of California, Davis and graduate student research fellowship from American Association of Textile Chemist and Colorist, and are grateful to Columbian Chemicals Co. for supplying CB nanoparticles.

References

[1] Fan QG, Ugbolue SC, Wilson AR, Dar YS, Yang YQ. AATCC Rev 2003;3:25.
[2] Li DP, Sun G. AATCC Rev 2003;3:19.
[3] Brady PR. Rev Prog Color 1992;22:58.
[4] Zhang M, Yudasaka M, Iijima S. J Phys Chem B 2004;108:149.
[5] Qin SH, Qin DQ, Ford WT, Resasco DE, Herrera JE. J Am Chem Soc 2004;126:170.
[6] Mawhinney DB, Naumenko V, Kuznetsova A, Yates Jr JT, Liu J, Smalley RE. J Am Chem Soc 2000;122:238.
[7] Pompeo F, Resasco DE. Nano Lett 2002;2:369.
[8] Liu J, Rinzler AG, Dai H, Hafner JH, Bradley RK, Boul PJ, et al. Science 1998;280:1253.
[9] Bower C, Kleinhammes A, Wu Y, Zhou O. Chem Phys Lett 1998;288:481.
[10] Poirier N, Derenne S, Rouzaud JN, Largeau C, Mariotti A, Balesdent J, et al. Org Geochem 2000;31:813.
[11] Ortega IK, Escribano R, Fernández D, Herrero VJ, Maté B, Medialdea A, et al. Chem Phys Lett 2003;378:218.
[12] Welham A. J Soc Dyers Colour 2000;116:140.
[13] Broadbent AD. Basic principles of textile coloration. Bradford: Society of Dyers and Colourists; 2000. p. 297.
[14] El-Shishtawy RM, Kame MM. Chem Eng Technol 2002;25:849.