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Coloration of textiles with self-dispersible carbon black nanoparticles

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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

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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.