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Dyeing of Polyester with Pristine Multiwalled Carbon Nanotubes

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ABSTRACT
Pristine Multiwalled Carbon nanotubes (MWNT) were dispersed in two selected surfactants and their mixture using a probe sonicator at room temperature. The results presented in this article apply only to the short-length MWNT. The dispersions achieved generally ranged from very poor to average. In the average category, the solvents ranked o-Dichloro benzene > Dimethyl formamide > Tetrahydrofuran. The surfactants and one of the mixtures performed better than average with Sodium lauroamphoacetate (Miranol) > Cetyl pyridinium chloride (CPC) > Miranol/CPC mixture (50:50). The higher the aspect ratio, the more difficult they are to disperse; the shorter the nanotubes, the better and more uniform the dispersion obtained. Miranol was then applied (dyed) on Polyester fabrics and various chroma Characteristics obtained.

Keywords: *Dispersion; Solvent; Surfactant; Sonication; Mixture; Chroma*

INTRODUCTION

The great deal of interest devoted to the study of CNTs is due to their exceptionally unique collection of properties. Applied quantum chemistry, specifically, orbital hybridization best describes chemical bonding in CNTs. The chemical bonding is composed entirely of Sp^2 bonds, similar to those of graphite. These bonds, which are stronger than SP^3 bonds found in alkanes, diamond and other materials from saturated bonding, provide them with unique mechanical, thermal and electrical properties. These properties confer on them great potentials in general nanotechnology applications especially optics and electronics [1, 2, 3, 4].

CNTs produced by catalytic carbon vapour deposition (CVD) grow in wavy, entangled assemblies which hold them together mechanically [5]. Although they do not possess reactive groups such as –OH, $–NH_2$, –COOH on their surfaces or ends, strong electrostatic forces keep CNTs together: van der Waals forces acting on a high surface area, e.g. 300 m^2/g [6, 7]. In addition, the absence of reactive groups makes them relatively inert in much the same way as graphene. Consequently, in the pristine form, they do not classically dissolve, but form poor dispersions in solvents - a distribution of particles which lack the capacity to form a homogenous mixture composed of only one continuous phase.

The ability to disperse them will therefore depend on their purity, aspect ratio, method of preparation, solvent employed and the type and duration of mechanical agitation.

Achievement of a good dispersion is a prerequisite for improving the performance of any composite, but this has yet to be satisfactorily achieved in CNTs [6, 7, 8]. This challenge is partly responsible for the inability to obtain optimum materials' property enhancement.

The methods of dispersing CNTs can be classified into two main categories; the physical technique, which involves the use of high power direct mixing operations without the modification of the CNT structure. The most common of these are high shear mixing, triple roll milling, ultra-sonication and melt mixing.

Apart from mild ultra-sonication, all these techniques are rather aggressive, causing breakages and rupture of the CNT structure, leading to shorter tubes with lower aspect ratios, and a significantly lower capacity for property-enhancement.

The chemical technique, which involves CNT surface modification, can further be grouped into two: Functionalization and use of surfactants. Functionalization involves the chemical modification of the CNT by introducing reactive

species or groups, such as –OH,–NH_2, –COOH onto its structure using strong acids such as sulphuric, hydrochloric and nitric acids under rather harsh conditions. These reactive groups confer solubility and reactivity, but the CNTs would have been robbed of their inherent unique properties.

The second technique does not involve covalent chemical reaction and is therefore, not a permanent surface modification. This non-covalent surface modification employs surfactants and compatibilization polymers. These solvate the tubes, which then disperse more easily [5, 7].

On its part, polyester is relatively inert, and in fabric form, in most cases, disperse dyes are used to dye them, popularly by high temperature (exhaust) dyeing or carrier dyeing. In order not to tamper with the inherent qualities of the CNTs by chemicals normally employed in carrier dyeing, exhaust dyeing was selected as a suitable method by which CNTs could be applied onto the polyester fabric. In this study, an attempt was made to find better dispersants for CNTs and then assessing them by applying on polyester fabric.

EXPERIMENTAL

Materials

Long-length MWNTs prepared by catalytic carbon vapour deposition using Fe/Co catalysts (average length – 500 nm) and Short-length MWNTs ((≥ 95% purity) were obtained from US Research Nanomaterials Inc., Houston, Texas (US 4353): (length : 0.5 - 2.0 nm; the chemicals/reagents used were as listed in Tables 2.1. The Ahiba nuance dyer was supplied by Datacolor International, U.S.A., and the probe by Misonix Inc., U.S.A.; The digital spectrophotometer (Spectralite III i7) was obtained from X-rite, U.S.A. The Plain woven 100 % Polyester (Dacron; 171 g/m²) was obtained from the Laboratory stores of TECS, College of Textiles, NCSU, USA. Its details are shown in Table 1.1.

Methods

Dispersion of MWNTs

The pristine *short-length* CNTs: 0.050g was placed in a 250mls stoppered flat-bottomed flask containing 100mls of the selected 1% surfactant in de-ionised water. This was then stirred for 30 mins using a probe sonicator operating at 550 watts at a frequency of 20 kHz at room temperature.

Application of CNTs on the fabric

High temperature (exhaust) dyeing method

(a) Baths with normal pH: The Ahiba Nuance top speed dyeing machine was used to dye the samples using standard high temperature (exhaust) dyeing techniques normally employed for 100% Polyester fabrics. It has 16 detachable, tight-lidded sample containers, uses infra-red (IR) heating with programmable dyeing temperature and rate of heating/cooling. Baths were prepared containing 1 (v/v) % of surfactant and 0.05 (w/v) % CNTs. Using a liquid-to-goods ratio (LR) of 50:1, 1 g of fabric was entered into individual sample containers at room temperature, and the machine set to increase at 20 °C/min up to a maximum of 130 °C. The agitation rate was 15 rpm. Dyeing was carried out at this temperature for 1 hr and then cooled to room temperature at a rate of 3°C/min. The same procedure was used to dye fabric pieces in the surfactant only (henceforth referred to as 'blank' or control)

(b) Baths with adjusted pH: The procedure in 3.3.1(a) was repeated, but with the pH of the baths adjusted first to 5, and then to 4 using 10 % acetic acid (to decrease the pH) and 10 % sodium carbonate (to increase it).

(c) Baths with adjusted pH and electrolyte (sodium chloride, NaCl): The procedure in 3.3.1(b) was repeated in the presence of NaCl (1 w/v) %

(c) ***Cold-padding:*** A bath was prepared containing 1 (v/v) % surfactant and 0.05 (w/v) % CNTs at a LR 20:1. with bath pH adjusted in the presence of the electrolyte. Fabric samples (1 g) were impregnated in this bath for 30 mins with occasional stirring, and the excess squeezed out at 20 % expression using a mini pad mangle. The results are shown in Fig. 1.1.

MWCNT application at different percent (%) shades One of the best surfactants used (Miranol) was selected and 1 g pieces of the fabric were dyed at 0.1 %, 0.5 %, 1 %, 2.5 %, 3.5 % and 5 % shades on weight of fabric (owf).The results are as shown in Fig. 2.1.

Reflectance spectroscopy

The equipment used is a digital spectrophotometer, Spectralite III-i7 model. It has the capacity to measure opacity/transparency, reflectance, transmittance/absorbance, gloss measurements, optical brightness as well as fluorescence of samples. It uses tri-beam

technology which allows the simultaneous measurements with the specular component included (SCI) and specular component excluded (SCE). It can be used to measure these characteristics in textiles, plastics, coated materials, liquids, optically brightened materials, etc. Essentially, it measures chromatic information based on the CIE L* a* b* colour scales. Since the test materials are textured, the equipment was set to take measurements with the specular component included (SCI).

The equipment was calibrated using a 6 mm aperture and the standard white and black discs under standard laboratory conditions. One after the other, the samples were mounted in front of the reflectance aperture and closed. The sample identification data was entered, the type of test and number of replications were selected in the CPU software and the test run.

To eliminate the reflectance of the substrate as a factor, the same function was determined for the 'blank' or control (which was 'blank' dyed) and the value for the control subtracted from that of the dyeing. The results are as indicated in Fig. 2.1 and Table 3.1.

RESULTS AND DISCUSSION

In dispersing the CNTs, only surfactant solutions were used so as not to interfere with their chemical constitution.

When CNTs were adequately dispersed, a black ink-like solution was obtained. This appearance suggests it can be used in dyeing, printing, painting or any such-like activities. Since the corresponding substrate is a fabric and making it electrically conductive is the goal, dyeing it with CNTs appears to be one of the best application methods of choice.

The polyester fabric absorbed the CNTs better with decrease in pH (optimally at pH 4) but better yet in the presence of an electrolyte (2 % owf). Exhaust dyeing gave poor, unlevelled results. It is noteworthy that higher temperatures are detrimental to the procedure as simple cold-padding at room temperature (27 °C) gave the best results.

The chromatic information was based on CIE L*a*b* colour scales. They include L* (lightness) which is on a 0-100 scale, 0 being completely black and 100 completely white; a* is redness (positive, 0°) to greenness (negative,180°); b* is yellowness (positive, 90°) to blueness (negative, 270°) ; C* (chroma, the colour saturation) from 0 (very dark) to 20 (very light); h° (hue angle, measure of the colour range between 0°-360°; going anti-clockwise on a flat plane from the cartesian co-ordinate abscissa, 0° = red, 90° = yellow, 180° = green, and 270° = blue).

For all the fabric samples, the higher the concentration of CNTs (owf), the lower the values of L* and C*, and the darker the shade, and vice-versa (Table 3). It also gave the Kubelka-Munk (K/S) values for determining additive reflectance for coloured objects [9, 10, 11].For all our samples, the K/S values increased with increase in concentration of CNTs (Fig. 3.1).

Table1.1: Fabric details

	Warp	**Weft**
Sett (threads/cm)	40.00	34.00
Yarn linear density (tex)	65.00	70.00
Yarn twist (turns/cm)	11.60	12.50
Crimp (%)	7.75	12.40

Table 2.1: Surfactants used

Surfactant	**Class of Surfactant**
Cetyl Pyridinium Chloride (CPC)	Cationic
Sodium Lauroamphoacetate (Miranol	Zwitterionic
CPC+Miranol (50:50)	Cationic+ Zwitterionic

Table 3.1: Chroma Characteristics of the fabric samples

Shade (%)	**C***	**L**
0.1	2.24	61.38
0.5	2.19	45.21
1.0	1.90	35.56
2.5	1.18	25.43
3.5	0.59	20.95
5.0	0.36	19.99

Fig. 1.1: Cold padding in acidic surfactant + electrolyte.

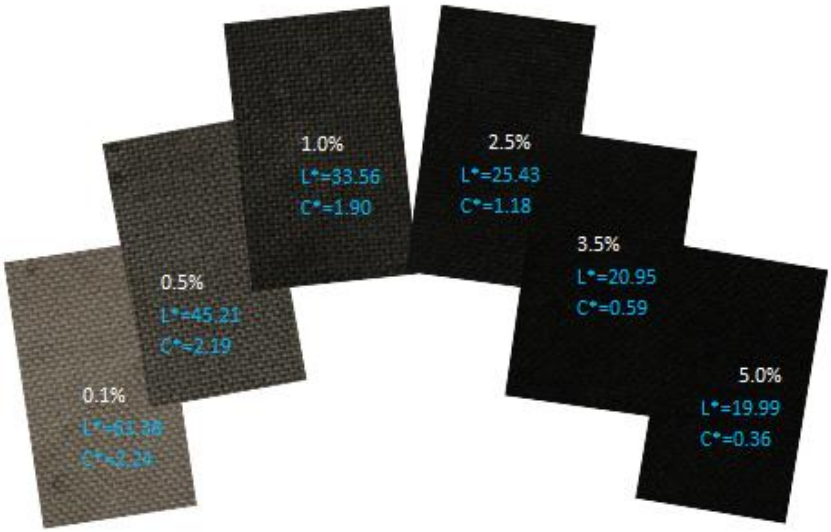

Fig. 2.1: CNT concentrations and their chroma characteristics.

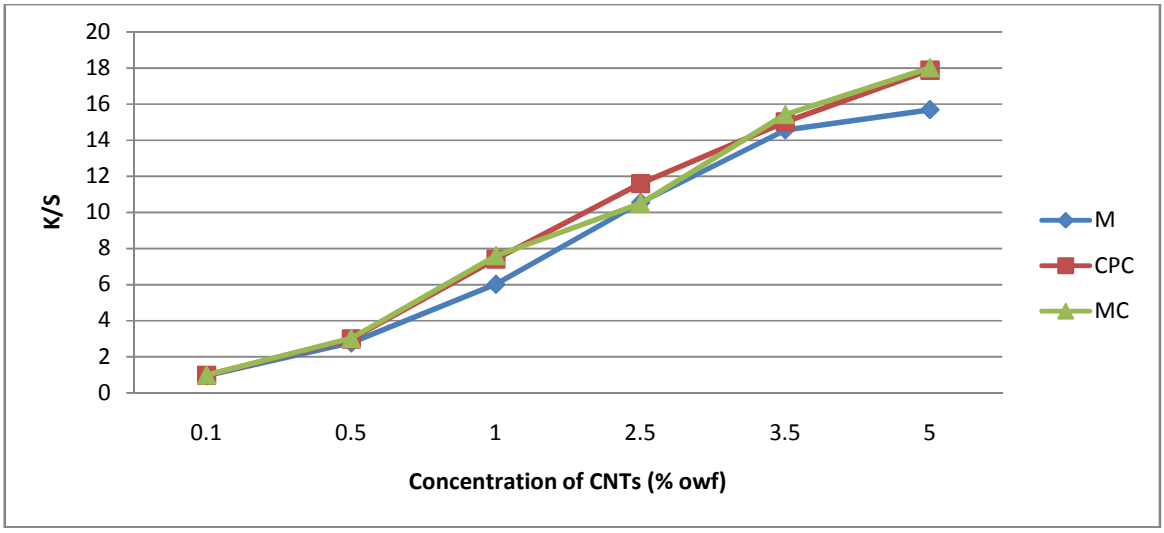

Fig. 3.1: K/S versus concentration for Miranol (M), CPC and their mixtures (MC).

CONCLUSION

Although CNT dispersions are dye-like solutions, they are not classical dyes and, therefore, should not be applied onto polyester fabrics as such. The 'exhaust' style, a typical, almost traditional method of dyeing polyester, did not yield good results. Miranol, CPC and their mixtures gave good dispersions for short periods of sonication. They were best applied on polyester fabrics by cold padding, especially short, drip-dry cycles in acidic dyebaths in the presence of an electrolyte. After curing, washing with water has very little noticeable effect on the dyed fabric.

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