ELECTRICAL CONDUCTIVITY OF POLYETHYLENE TEREPHTHALATE (PET) FABRIC FUNCTIONALIZED WITH MULTI-WALLED CARBON NANOTUBES

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ABSTRACT

Low aspect ratio pristine Multi-walled carbon nanotubes prepared by carbon vapour deposition (CVD) were dispersed in Miranol, Cetyl pyridinium chloride and a 50:50 ratio mixture of them. They were each applied on 100% PET fabric using classical polyester dyeing techniques (exhaust dyeing) as well as cold padding by 3, 5-minute dip-dry techniques under controlled conditions. Exhaust dyeing yielded poor, uneven uptake; cold padding gave good, level uptake. The chroma characteristics of the dyed fabrics conformed to the Kubelka-Munk equation for determining additive reflectance functions. The polyester fabric became electrically conductive at a percolation threshold between 1-2.5% shade (owf). The electrical conductivity increased with the concentration of carbon nanotubes, up to 5.0x10^{-3} S/m at 5 % shade concentration. From the percolation threshold onwards, the conductivity was able to power light-emitting diodes (LEDs).

Keywords: *Carbon nanotubes; sonication; dispersion; cold-padding; exhaustion; electrical conductivity.*

1. INTRODUCTION

In the last two decades, there has been increasing interest in new materials with unique characteristics. One of the most interesting is the demands placed on intelligent and multifunctional fibrous materials which have active functions in addition to traditional textile properties. The novel functions were imagined to be obtained by modifying the textile material or integrating the active component(s) into the textile structure. Textile structures on their part, are particularly suitable for this purpose because they possess the requisite structure, porosity, flexibility in addition to cheap and easy processability.

In particular, the demand for electrically conductive textiles is growing rapidly not only in relation to industrial needs such as sensing, electromagnetic interference (EMI) shielding, electrostatic discharge, data transfer in clothing, dust and germ-free clothing, corrosion protection, but also for military applications such as camouflage and stealth technology (Kim *et al.,* 2006).

As usual, it started with making a conductive polymer composite which will either be used as-constructed, or subsequently be fabricated into other preferred forms or articles. During this period, carbon nanotubes (CNTs) have established itself as a novel material with exceptionally unique collection of properties. Its nanometer dimensions (1 billionth or 10^{-9} m diameter) and high aspect ratio (up to 132,000,000:1) in addition to its high strength, modulus, flexibility, electrical and thermal conductivity as well as optical characteristics make them particularly suitable for reinforcement of metals, polymers and cceramics. Multi-walled carbon nanotubes (MWNTs) produced by catalytic carbon vapour deposition (CVD) grow in wavy, entangled assemblies which hold them together mechanically (Battisti, 2009). Although they do not poses 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 (Sahoo *et al.,* 2010; Choudhary and Gupta, 2011). 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.

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 (Fiedler *et al.*, 2005; Sahoo *et al.*, 2010; Chaudhary and Gupta, 2011). This challenge is partly responsible for the inability to obtain optimum materials' property enhancement.

On its part, Polyethylene terephthalate (polyester, PET) is the most common and popular member of the thermoplastic-polyester family, and is the third most-produced polymer, after polyethylene and polypropylene.

In its natural form and even after fibre extrusion and processing to yarns and fabrics, the polymer is saturated. This explains its relative inertness, hydrophobicity and therefore its low moisture regain, as well as resistance to chemicals. The issue of reinforcing this inert material with an equally inert carbon nanotubes has proved challenging over the past decade or so.

Recently, however, there have been reports of PET fibres prepared by electrospinning (Ahn et al., 2008) and melt-spinning PET incorporating acid-functionalized MWNTs (Yoo et al., 2012). In both cases, the fibres had improved electrical, thermal and mechanical properties.

2. Experimental

2.1 Materials and Reagents

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 3.1. Long-length MWNTs prepared by catalytic carbon vapour deposition using Fe/Co catalysts (average length – 500 nm) was obtained from TECS, College of Textiles, NCSU, USA. The short-length MWNTs was obtained from US Research Nanomaterials Inc., Houston, Texas (US 4353): (average length : 0.5 - 2.0 nm; Cetyl Pyridinium Chloride (CPC) was obtained from Sigma-Aldrich, U.S.A. and Sodium Lauroamphoacetate (Miranol) fom Rhodia, U.S.A.

3. Methods

3.1 Preparatory experimental procedures

3.1.1 Fabric Scouring

The polyester fabric was scoured at 100°C for 30 mins in a bath containing 2g/l non-ionic surfactant (Primasol NMB) and 2g/l soda ash at a LR 50:1; It was rinsed copiously with water and dried.

3.1.2 Dispersion of CNTs

(a) 0.025g of the pristine *long-length* CNTs was placed in a 100mls stoppered flat-bottomed flask containing 50mls of 1% surfactant in de-ionised water (CPC, Miranol or their 50:50 ratio mixtures). This was then stirred for 30 mins using a probe sonicator (Misonix model XL 2020) operating at 550 watts at a frequency of 20 kHz at room temperature.

(b) The same procedure as in (a) was repeated with pristine *short-length* CNTs.

3.2 Application of CNTs on the fabric

3.2.1 High temperature (exhaust) dyeing method

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 they could be applied onto the polyester fabric.

(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 was programmed 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 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 3.2.1(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 3.2.1(b) was repeated in the presence of NaCl (1 w/v) %.

3.2.2 Cold-padding

A bath was prepared containing 1 (v/v) % surfactant and 0.05 (w/v) % CNTs at a LR 20:1.
Fabric samples (1 g) were impregnated in this bath for 5 mins with occasional stirring, removed and squeezed. This was repeated 3 times. On the third time, the excess was squeezed out at 20 % expression using a mini pad mangle.

This was repeated (i) with bath pH adjusted and (ii) with bath pH adjusted in the presence of the electrolyte. The results are as shown in Fig. 4.

4. Analytical techniques

Unless otherwise stated, all analyses were carried out under standard conditions of testing textile materials (ASTM International D 1776 - conditioning at 21±1°C, 65±2% relative humidity for 4 hours)

4.1. Reflectance spectroscopy

The equipment used is a digital spectrophotometer, Spectralite III-i7 model, supplied by x-rite, USA. Essentially, it measures chromatic information based on the CIE L* a* b* colour scales.

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 to remove the effects of the the control from the other dependent variables, and the test run. The results are shown in Fig.

4.2. Field-emission scanning electron microscopy (FE-SEM)

The FE-SEM equipment used was obtained from Phenom Nanoscience Instruments Inc.. It was used to examine the surface morphology of the fabric samples at various magnifications. The ultra-high resolution equipment required that samples should be conductive, otherwise they needed to be coated with a conducting material. The control sample (non-conductive) was first gold-sputtered in an accessory chamber for 10 mins before mounting in the analyzer. In the analyzer, the sample surface was scanned through various magnifications until the right resolution was obtained; the images were then captured.

4.3. Electrical Conductivity Measurements

Three types of equipment were used:

(a) The 2-point probe, Metex auto/manual range dual display digital multimeter with PC interface (M-3860D) by Metex, USA, was used to measure the resistance between two probes separated by selected distances apart.

(b) The 4-point probe, consisting of Keithley 6221 DC and AC current source and a Keithley 2182A Nanovoltmeter using a current range ± 20 E-6 ($\pm 20x10^{-6}$ A) and a voltage range of 10 V that automatically takes and averages 250 readings. It was used to measure surface and bulk resistivity in high-resistance substrates over each square unit centimeter or volume.

4. RESULTS AND DISCUSSION

4.1 Dispersion of CNTs

In this report, only the effects of surfactants are considered, being the only solvents that do not classically react chemically with carbon nanotubes. At first, long nanotubes were used. Their nanoscale dimensions and high aspect ratio made them more difficult to disperse, since as the surface area increases, so does the attractive forces between aggregates. In addition, each flexible tube associates with its neighbours over a longer length, and is more likely to get entangled and aggregate in a liquid medium when left undisturbed, compared to shorter tubes. It is logical to assume that media that can appreciably disperse long tubes will invariably perform better with shorter tubes which was confirmed in this work. When shorter tubes were used, a reasonably better dispersion was achieved which could remain stable for at least one week.

In this case the surfactants were ranked Miranol (Zwitterionic)>CPC (cationic) >CPC/Miranol mixture.

The adsorption of surfactants into inorganic and organic surfaces usually depends on the chemical characteristics of the particles, surfactant molecules, the solvent, concentration of the surfactant, electrolyte, pH, temperature, etc. (Vaisman *et al*., 2006; Zhang and Somasundaran, 2006).

The driving force for the adsorption of ionic (cationic and anionic) on charged surfaces is the coulombic or electrostatic interactions e.g. between the surfactant's positively- or negatively-charged head group and the negatively- or positively-charged surface (CPC is a cationic quaternary ammonium compound); the mechanism by which non-ionic surfactants adsorb onto a hydrophobic surface is based on a strong attraction between the solid surface and the surfactant's hydrophobic tail, including hydrogen bonding or non-polar interactions. Miranol is zwitterionic (has two quarternary amino groups, $-COO^{-}$ Na^{+} and –OH). Zwitterionics are amphoteric, and therefore, behave basically like non-ionics, but can also behave like the cationics or anionics, depending on the pH of the solution. Hydrogen bonding between surfactant species and the solid surface species could occur in systems containing hydroxyl, phenolic, carboxylic and amine groups on the surfactant. Other forces include lateral associative interaction, solvation, and desolvation (Zhang and Somasundaran, 2006).

4.2 Application of CNTs on the fabric

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.

5.2.1 High temperature (exhaust) dyeing

From available reports (Battisti, 2009; Sahoo *et al*., 2010; Chaudhary and Gupta, 2011) and experience during dispersion, the length of the nanotubes is a major contributor to poor dispersibility, and could therefore be to uniform application and distribution on the fabric. This is responsible for the patchy and unlevel dyeing obtained and, therefore the need to opt for shorter nanotubes.

Shorter nanotubes gave better dispersions, and were applied first in acidic conditions of different severities (pH 4 and 5). It was observed that some surfactants create a better dyeing environment in more acidic conditions (e.g. Miranol and CPC; pH 4). This condition also proved better than application in the surfactant's natural pH (unadjusted). Deeper shades were obtained in acidic conditions, but addition of NaCl in the acidic bath further improved both shade and levelness.

Cold padding, however, gave better and more level dyeing under the same bath conditions. With shorter dip-dry times, it eliminates the application of high temperature and its associated equipment and other controls.

This explains why this technique was subsequently adopted as the application method of choice for all the fabric samples.

Acidic dyebath conditions tend to improve absorption of the CNTs. Dyeing of polyester had always preferred acidic conditions, but our peculiar case corroborates the work of Gonçalves (Gonçalves *et al.,* 2012) who functionalized MWNTs with oxygen-containing surface groups and incorporated them into cotton and polyester fabrics by a process similar to traditional industrial dyeing. He concluded that the incorporation efficiency was higher in acidic conditions. The presence of an electrolyte actually improves levelness. This is consistent with the traditional role of electrolytes in textile dyeing operations, and is particularly important because the more niform the application, the better and more consistent the fabric properties-enhancement.

4.2.3 Application at different shades

From the results obtained in section 4.2.2, one of the surfactants (Miranol) was selected, mainly due to its lower cost and availability, and was used to dye 1 g pieces of fabric to 0.1 %, 0.5 %, 1 %, 2.5 %, 3.5 % and 5 % shades (owf). The results, along with their corresponding chroma characteristics are as shown in Plate XXVIII.

4.3 Analytical techniques

4.3.1 Reflectance spectroscopy

The transmittance/absorbance of the dispersions before and after dyeing could not be measured because black solutions usually absorb all the uv-visible radiation passed through them and transmit none for detection and measurement. The chromatic information obtained using the digital spectrophotometer are shown in Figs.5 and 6.

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 (Plate XXVIII). It also gave the Kubelka-Munk (K/S) values for determining additive reflectance for coloured objects. For all our samples, the K/S values increased with increase in concentration of CNTs (Figs. 4.1 and 4.2).

4.3.2 Field emission scanning electron microscopy (FE-SEM)

Plate XXIX shows a micrograph of the control sample magnified 1000 times. Figs 7b and 7c present the fabrics processed in 3.5 % Miranol and CPC respectively, at the same magnification. The FE-SEM images of the plain and the dyed polyester samples are shown in Fig. 7. The control fabric shows long, lustrous, even shiny filaments running along the yarns without any discontinuity along their lengths. There is also no sign of broken fibre heads or ends within the micrograph (Fig. 7a); this is an indication that the fabric was made from continuous filament yarns, not staple. The micrograph of the dyed fabric (Fig. 7a and 7b showed that all the lustre had been eliminated from the fibres. This suggests that some of the CNTs actually penetrated into the filaments, and of course, a larger percentage can be seen coating the filaments and also lodged between their interstices. This corroborates the results from the work of Fugetsu *et al*., (2009) who impregnated polyester multifilaments in MWNTs dispersed in a mixture of zwitterionic and anionic surfactants. SEM images revealed a CNT-skin, with the CNTs arranged in continuously interconnected networks over the surfaces of the filaments, which functions as the electrically conductive layer (ECL).

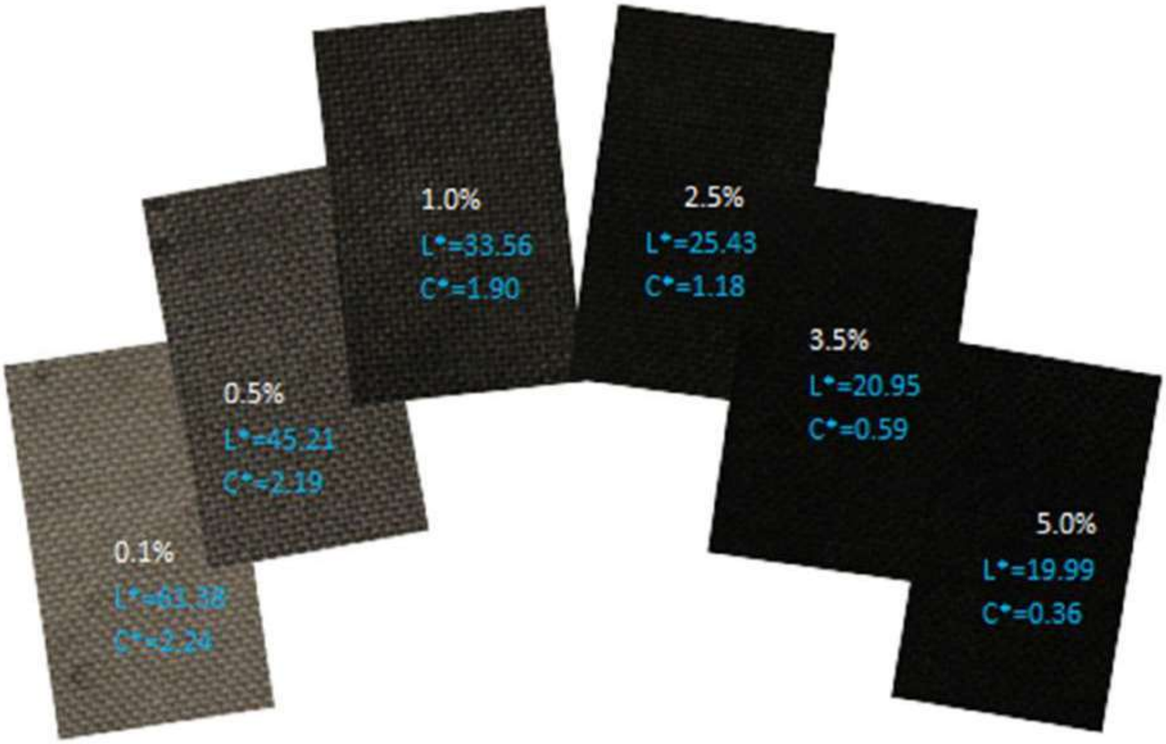

Fig. 5: CNT concentrations and their chroma characteristics.

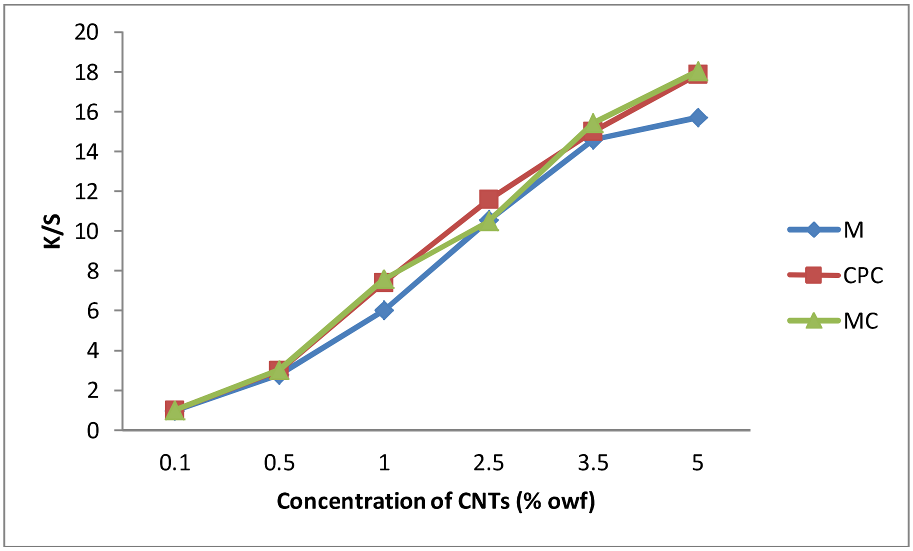

Fig. 6: K/S versus concentration for Miranol (M), CPC and their mixtures (MC).

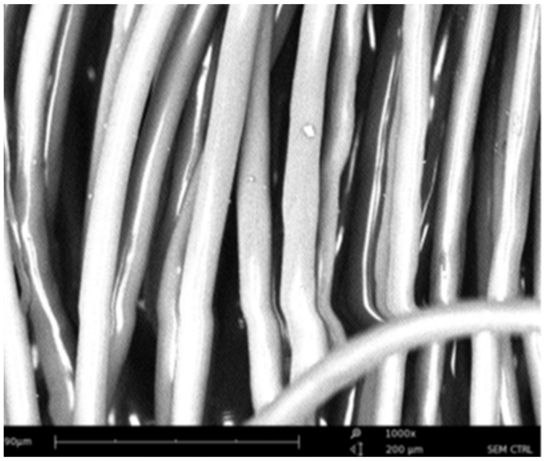

Fig. 7a: FE-SEM micrographs of the control sample.

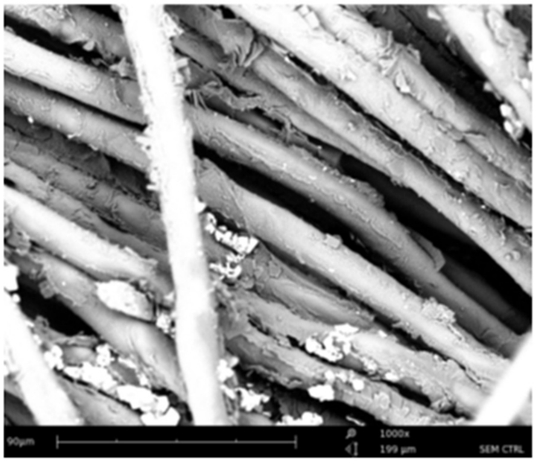

Fig. 7b: FE-SEM micrographs of fabric treated with 3.5% Miranol.

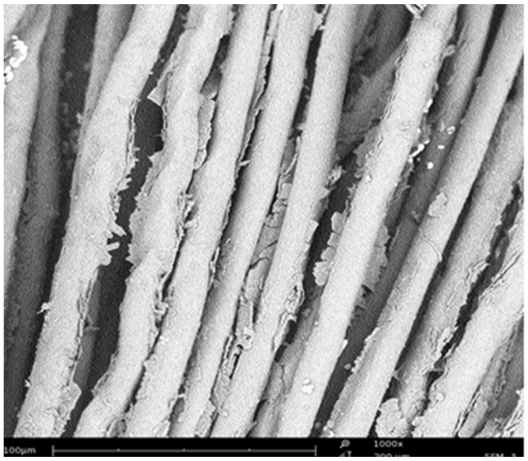

Fig. 7c: FE-SEM micrographs of fabric treated with 3.5% CPC.

4.3.3 Electrical properties

Figs.4.3 and 4.4 show the variation of resistivity with type of surfactant in the warp and weft directions respectively. Except for MC, adjusting the pH to acidic conditions and introducing NaCl into the bath significantly reduced the resistivity.

In each case, the peaks for S, SP and SPE are displayed for the warp and weft direction; all of them show evidence of the large difference between application in S only on one hand, and application in SP and SPE on the other,
where S – surfactant only;
SP – surfactant in adjusted pH;
SPE – surfactant, adjusted pH + electrolyte
M – Miranol;
C – CPC (Cetyl pyridinium chloride);
MC – Mixture of M and C (50:50);
Wa or wa – warp; and
We or we – weft.

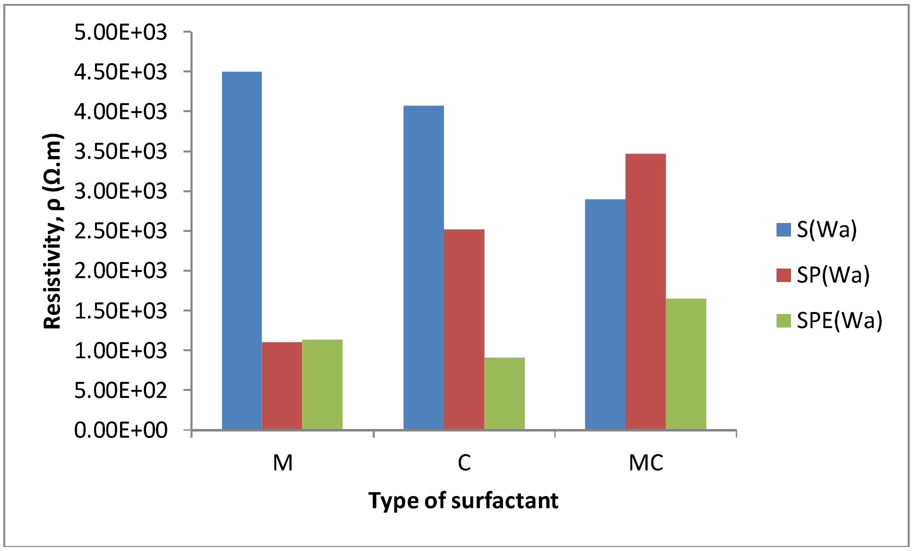

Fig. 8a: Variation of resistivity with type of surfactant (warp direction).

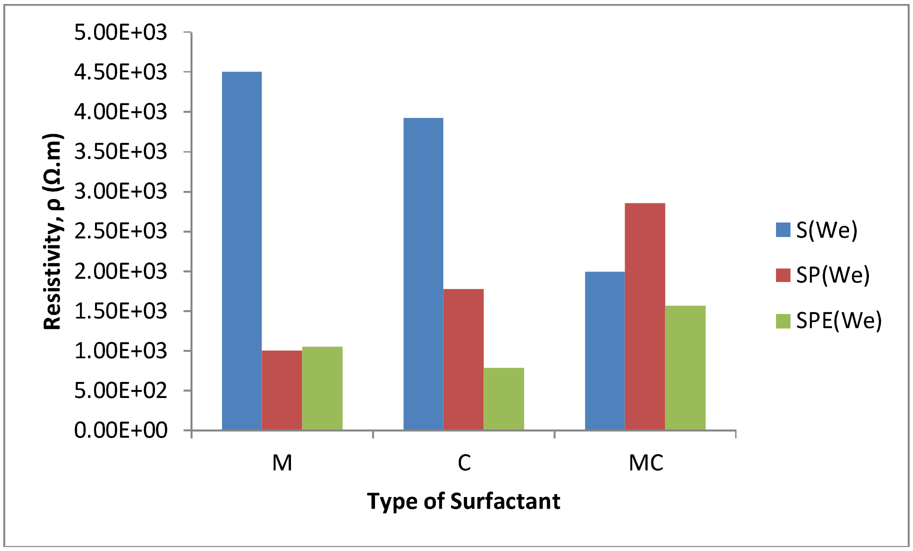

Fig. 8b: Variation of resistivity with type of surfactant (weft direction).

The electrical resistivity of the samples dyed from 0.1-5% owf were measured using the 2-point probe at a probe separation of 3 cm, and the results for both the warp and weft directions are shown in Fig. 4.11. The resistivity, ρ, decreased with increase in the concentration of the CNTs. This implies an increase in conductivity, σ, in the same manner. The bulk resistivity, ρ and conductivity, σ, are related by the equation

$$\sigma = \left({}^{1}/_{\rho t}\right) \cdots \cdots \text{eq. 1}$$

where t is the thickness of the material.

It should be noted that the actual height/peak of the histogram for 0.1 - 1.0 % owf could not be shown on this graph because they will practically dwarf or diminish those of 2.5 - 5.0 %, so that they will appear as zero.

On the same graph, it can be observed that there is a sharp drop in resistivity between 1 % and 2.5 %. This region highlighted the percolation threshold - the critical concentration above which electrical conductivity started manifesting in the fabrics. After the percolation threshold, conductivity increased with increase in the concentration of CNTs, up to a maximum of 5.5-6 % (owf), after which the fabric ceases to absorb more nanotubes.

In Fig. 8, the resistivities were highest when only surfactants were used, decreased in acidic conditions and was least when surfactants were used in acidic conditions in the presence of an electrolyte. CPC gave the least resistivity, followed by Miranol and then their mixture.

It is noteworthy that in Figs. 8, the actual peak value of the resistances for Miranol could not be adequately fitted on these graphs because they are much higher than the others in such a way that representing them together will diminish the value of the others to almost zero.

Fig. 10a and b show the variation in the bulk resistivity from control to 5% (owf). In (a) the values for 2.5 – 5% are much smaller than the control so that they appear to be zero, but (b) shows the magnified relationship between 2.5 – 5%, while (c) shows the corresponding conductivity from the control to 5% (owf)

The conductivity achieved was through a network of conductive pathways generated by the CNTs when adjacent tubes are in contact. The statistical chances of forming these conductive pathways increases with the concentration of the CNTs. In addition, there is a considerable body of evidence suggesting the presence of an insulating layer between the nanotube particles even above the percolation threshold, just as is the case for other types of conductive fillers (Grossiord *et al.*, 2008). This implies that the percolating nanotubes may not necessarily be in actual contact with each other and that conductivity may occur via some tunneling or hopping process through the insulating layer separating them. This can only happen if the distance between two neighbouring tubes is below a certain critical value (Grossiord *et al.*, 2008).

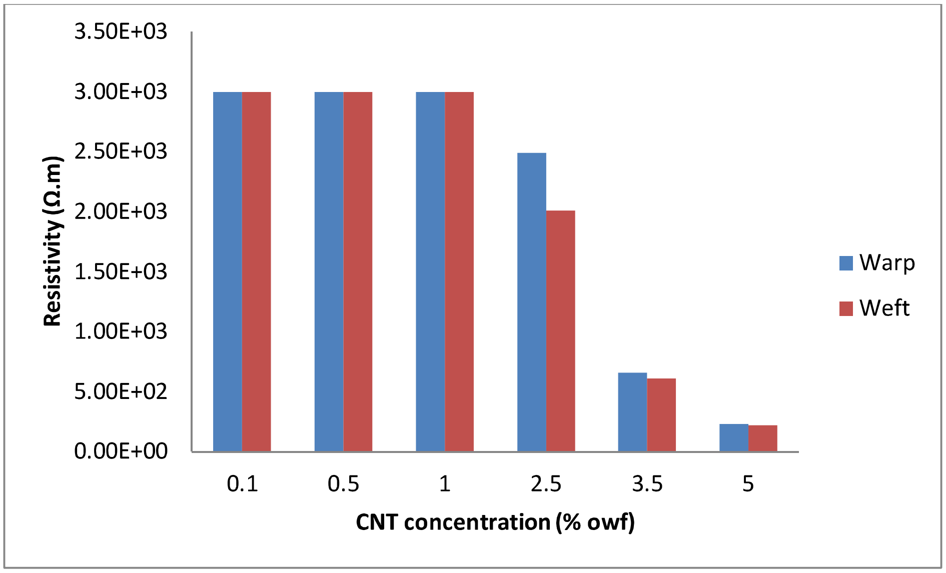

Fig. 9: Resistivity as a function of CNT concentration (Miranol).

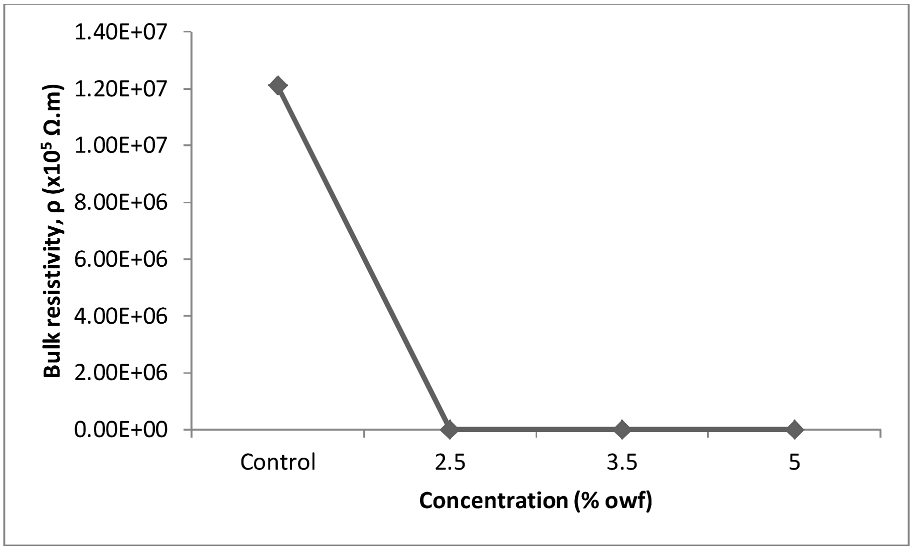

Fig. 10a: Bulk resistivity, ρ, as a function of concentration (% owf).

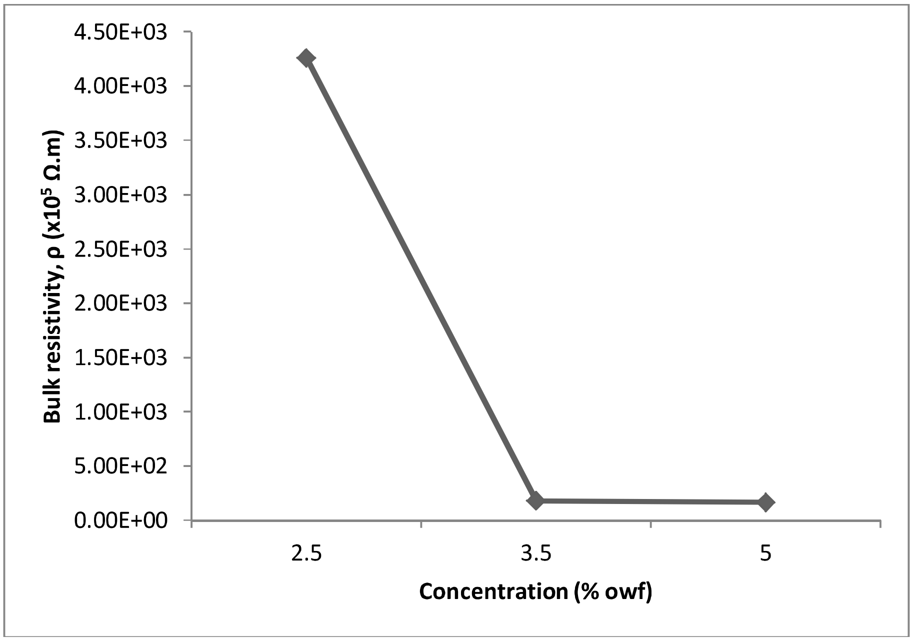

Fig. 10b: Bulk resistivity, ρ, as a function of concentration (% owf).

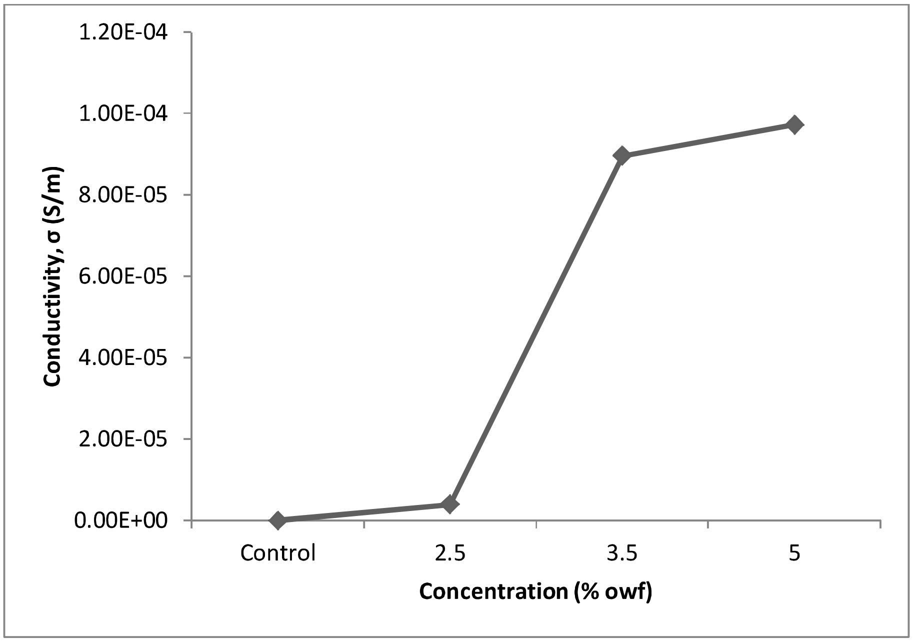

Fig. 10c: Conductivity, σ, as a function of concentration (% owf).

6.1 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. For all the 3 surfactants used, the polyester fabric was made electrically conductive. The electrical conductivity obtained varied with the type of surfactant: CPC>Miranol>Miranol+CPC. Miranol, the statistical median of the 3-reagent observations, had a percolation threshold of between 1-2.5% (owf). This implies that the percolation threshold of CPC was less than that of Miranol (1-2.5%), while that of a mixture of Miranol and CPC was greater than that of Miranol. The dyed fabric exhibited good electrical conductivity in the region of 5.0×10^{-3} S/m. After the percolation threshold, conductivity increased with increase in the concentration of CNTs, just as demonstrated in other composites involving pristine nanotubes (Sun *et al.*, 2013), up to a maximum of 5.5-6% (owf), after which the fabric ceased to absorb more nanotubes. The electrical behaviour of the fabric was found to vary in a similar way as that of metals i.e., the resistivity or conductivity varies with the length of the conductor.

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