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Synergizing the Electrical Conductivity of Functionalized Woven Polyester (PET) with In-Situ Polymerization of Aniline

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ABSTRACT

Polyester fabric (100%) was electrically functionalized by dyeing in pristine multi-walled carbon nanotubes in Miranol at different shades (0.1 - 6.0) % (owf). Aniline was then polymerized within each of the fabric samples using Sulphuric acid and Potassium peroxydisulphate at oxidant: monomer ratio 1.25 and LR 40:1. After polymerization, the conductivity percolation threshold reduced from 1.0 – 2.5 % to 0.5 – 1.0 % shade (owf) and the electrical conductivity increased by at least 14 orders of magnitude. At 5% shade, the conductivity was 1.0 x 10^{-4} S/cm, from a control material with 1.2 x 10^{12} Ω.m resistivity. Comparing 1.0 % and 3.5 %, the difference in conductivity was 680 orders of magnitude.

Keywords: *Carbon nanotubes; Monomer; Oxidant; Impregnation; Polymerization; Percolation threshold; electrical conductivity.*

Introduction

The last three decades have recorded increased interest and activity in intelligent and multifunctional fibrous materials which have active functions in addition to their traditional properties. 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; Iliya *et al.*, 2015). The novel functions were obtained by modifying the textile material or integrating 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 this area, 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 ceramics.

Polyaniline is outstanding, due to its thermal, environmental and chemical stability, low cost and easy synthesis (Kim *et al.,* 2006; Kutanis *et al.,* 2006). In this report, polyester was plasma treated, dyed with pristine multi-walled nanotubes and then aniline was polymerized on the dyed material.

Experimental

Materials and Reagents

Plain woven 100 % Polyester (Dacron, 171 g/m²), previously scoured, plasma-treated and dyed with multi-walled carbon nanotubes (MWNTs) from US Research Nanomaterials Inc., Houston, Texas (US 4353); (Purity: > 95 %; average length: 0.5 - 2.0 nm) in Sodium Lauroamphoacetate (Miranol, from Rhodia, USA); Other chemicals were obtained from Sigma-Aldrich, USA, and were used as sourced; 2-ponit probe auto/manual digital multimeter was obtained from Metex, USA. Other Fabic details are as obtained in table 5.1.

Methods

Polymerization of Aniline on the fabric

Polymerization of Aniline (Kutanis *et al.,* 2006; Neelakandan, 2009; Molina, 2011; Iliya,2015). In a 250 ml flat-bottomed flask, 0.3 M aniline (monomer) was stirred in 0.25 M H_2SO_4 for 10 mins. 1 g of the fabric was impregnated in this solution at room temperature for 30 mins with mild agitation. Pre-cooled Potassium peroxydisulphate (oxidant) was added slowly to initiate polymerization (oxidant:monomer ratio, 1.25; LR 40:1). Polymerization was allowed for 3 hrs and then the fabric was removed and washed with aqueous 0.25 M H_2SO_4 in a beaker (to remove loose polymer, unconsumed monomer and oxidant). This was then filtered through a previously weighed sintered crucible filter and the residue washed with deionized water

before drying. Both fabric and the residual polymer were conditioned and weighed.

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).

Reflectance spectroscopy

The equipment used is a digital spectrophotometer, Spectralite III-i7 model. It has the capacity to measure opacity/transparency, reflectance, transmittance and/or 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.

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.

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.

Electrical characteristics

(a) 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 ($\pm 20 \times 10^{-6}$) 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.

(b) The Keithley 8009 resistivity test fixture and Keithley 6517B electrometer/high resistance meter, used to measure bulk resistivity of sheet materials.

Tensile characteristics

The raveled strip test was carried out in the warp and weft directions using a constant rate of extension (CRE) Instron automatic testing machine with an IBM computer interface and printer according to the ASTM International D 5035-11. The average breaking force, percent elongation at break, work of rupture was measured for the various samples.

Abrasion characteristics

The Martindale abrasion tester was used to measure the abrasion resistance of the fabrics according to the ASTM International standards ASTM 4966-12$^{\varepsilon 1}$. The standard abradant used was a plain woven cross-bred worsted wool fabric (Heal's Martindale abradant fabric SM25). The polyurethane foam backing was of 3±0.01mm thickness, 29-31 g/m^3 density, and 170-210 hardness. 38 mm and 140 mm diameter press cutters were used to cut the fabrics and the AATCC Grey scale for colour change was used to evaluate the change of colour after abrading.

Results and discussion

Table 5.1: Fabric details

Properties	Warp	Weft
Sett (threads/cm)	40.00	34.00
Linear density (tex)	65.00	70.00
Twist (turns/cm)	11.60	12.50
Crimp (%)	7.75	12.40

Reflectance Spectroscopy

The digital spectrophotometer used was calibrated to measure reflectance properties of the fabric with the specular component included (SCI). 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. Also, the digital spectrophotometer used automatically generated values for K/S. For all our samples, the K/S values increased with increase in concentration of CNTs, just as is common with classical dyes. The widely known Kubelka-Munk equation is used for determining additive reflectance functions for coloured objects; it also represents the colour strength or yield, recorded at the wavelength of maximum absorption. It is an expression which relates the absorption (K) and scattering (S) coefficients of incident light with reflectance (eq. 4.1) or the concentration (eq. 4.2) of the dyeing (owf).

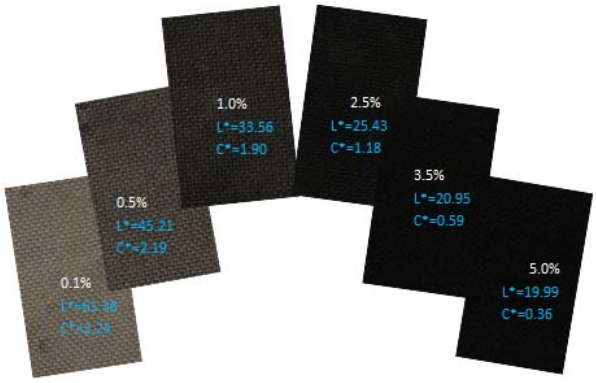

Fig. 5.2.1: CNT concentration (owf) and their chroma characteristics

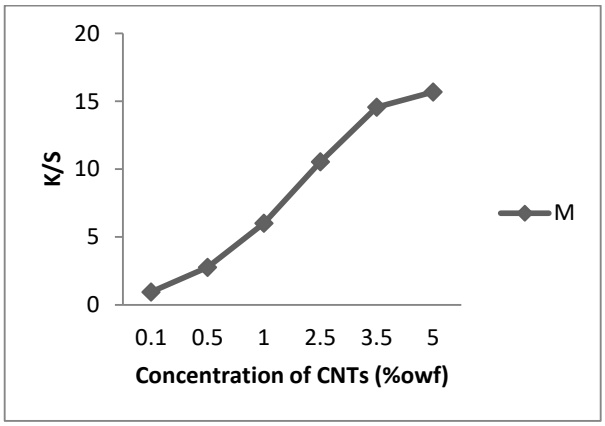

Fig. 5.2.2: K/S as a function of concentration of CNTs for Miranol (M).

If the % reflectance (R %) of a dyed material at any wavelength (but normally the wavelength of minimum reflectance or wavelength of maximum absorption) relative to that of a perfect white diffuser (100 %, which was used for the calibration) – or, alternatively, the fractional reflectance, r, when that of the perfect white diffuser is 1, then

$$K/S\,(dyeing) = \frac{(1-r)^2}{2r} = \frac{(100-R)^2}{200R} \cdots\cdots eq.5.2.1$$

(Aspland, 1997).

Standard colours (perfect white and black) were used to calibrate reflectance with the specular component included (SCI). 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, so that

$$\frac{K}{S(dye)} = \frac{K}{S(dyeing)} - \frac{K}{S(substrate)}$$

$$= S.C(at\ low\ c\ values) \cdots\cdots eq.5.2.2$$

where C is the concentration of CNTs and S is the slope of the graph of K/S versus concentration when the best straight line is fitted through the points. Once the K/S reflectance function has been corrected, the result is a function which resembles the absorbance function for dye solutions, and which at low concentrations of the dye (owf), is approximately a linear function of the dye concentration. Since the K/S values increased with increase in concentration of CNTs, this may suggest that CNTs have a certain tincture of dyes. It is suspected that this K/S concordance is due the fact that at no time in the application of the nanotubes did the fabric become fully black (so that it cannot reflect any light); they were only shades of black and must therefore exhibit some level of reflective qualities. It is suggested that this was responsible for the results obtained.

Field-emmission Scanning electron Microscopy (FE-SEM)

Fig. 1 shows a micrograph of the control sample magnified 1000 times and Fig. 2 that of a CNT-dyed fabric on which aniline was polymerized in-situ rendered in 1000th order of magnification. They show polyaniline deposited as a spongy microfilm within the fabric.

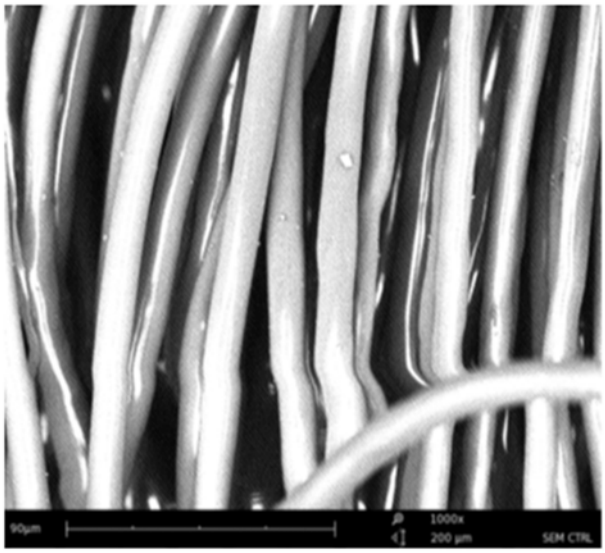

Fig. 1: FE-SEMmicrographs of the control sample (100% polyester fabric)

Electrical characteristics

Fig. 1 shows the variation of resistivity with concentration of CNTs. It was very high (out of the range of the equipment used) for 0.1 – 1 %, dropped sharply from then to 2.5 % and continued as the concentration increased.

Fig. 2: FE-SEM micrographs of polymerized Aniline on the fabric (magnified X 1000)

Fig. 2 is the plot for bulk resistivity, ρ, as a function of concentration of CNTs. It was very high for the control sample (over 1.2 x 10^{12} Ω.m) but dropped sharply as the concentration increased to 2.5 %; it gives the impression that the resistivity is zero from a concentration of 2.5% upwards. This, however, is not the case. The large difference between the resistivities of the undyed and dyed fabrics simply diminished the values for the dyed.

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. It is 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.

Isolating the values for dyed samples only, and plotting them against their respective CNT concentrations, the graph is as shown presented in Fig. 3. The conductivity, σ, corresponding to the resistivity shown in Fig. 3 is presented in Fig. 4.

After polymerization of aniline, washing drying and conditioning, a 2-point probe, METEX auto/manual range dual display digital multimeter with PC interface (M-3860D), was used to measure the resistance between two probes separated by a known distance. The results for fabrics dyed with CNTs only and those dyed and then treated in PANI are as shown for three different probe separation distances (1,2 and 3cm) in Figs. 6 and 7 respectively.

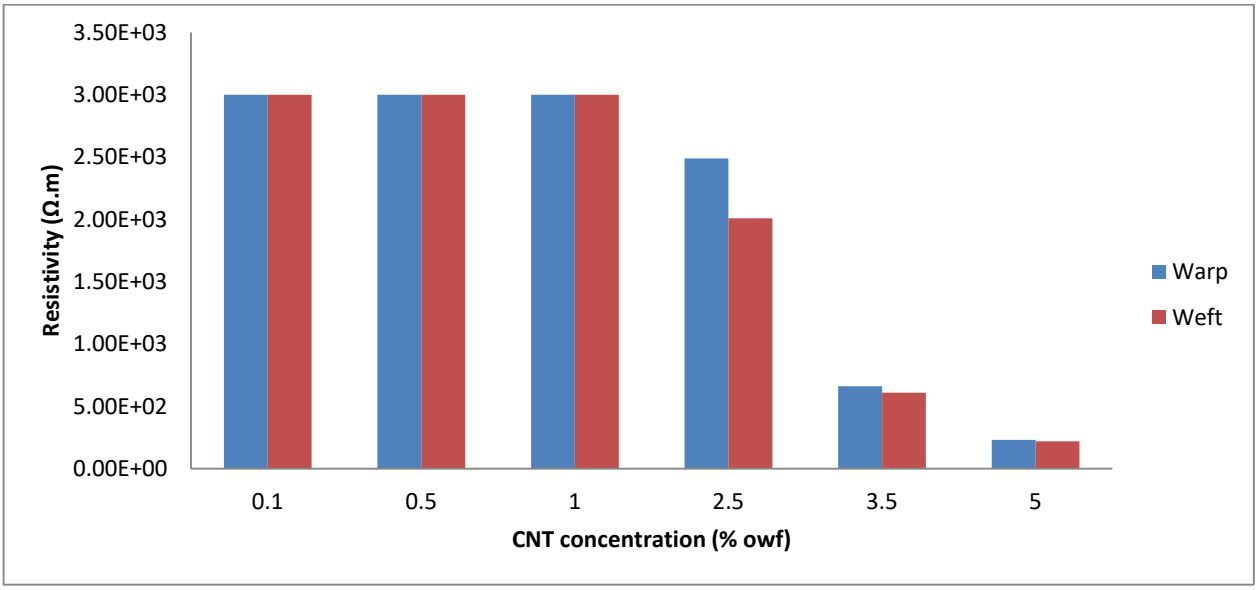

Fig. 1: Resistivity as a function of CNT concentration (Miranol).

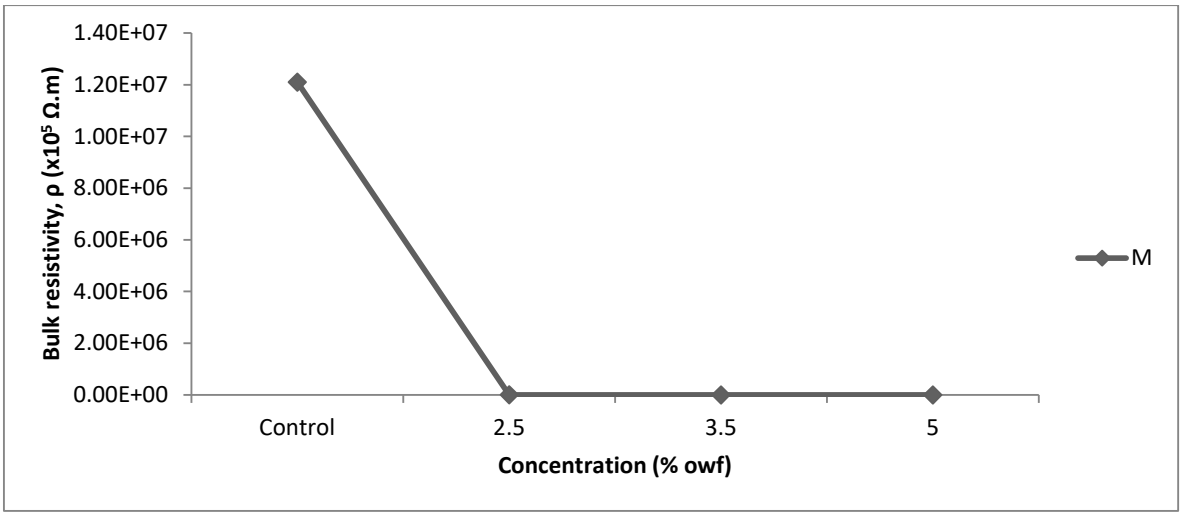

Fig. 2: Bulk resistivity, ρ, as a function of concentration (% owf).

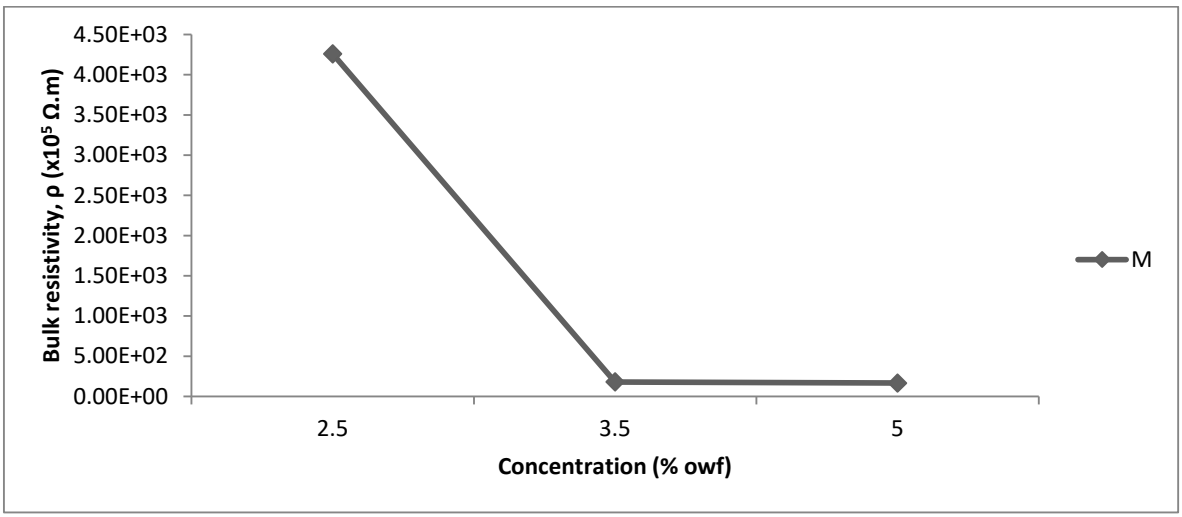

Fig. 3: Bulk resistivity, ρ, as a function of concentration (% owf).

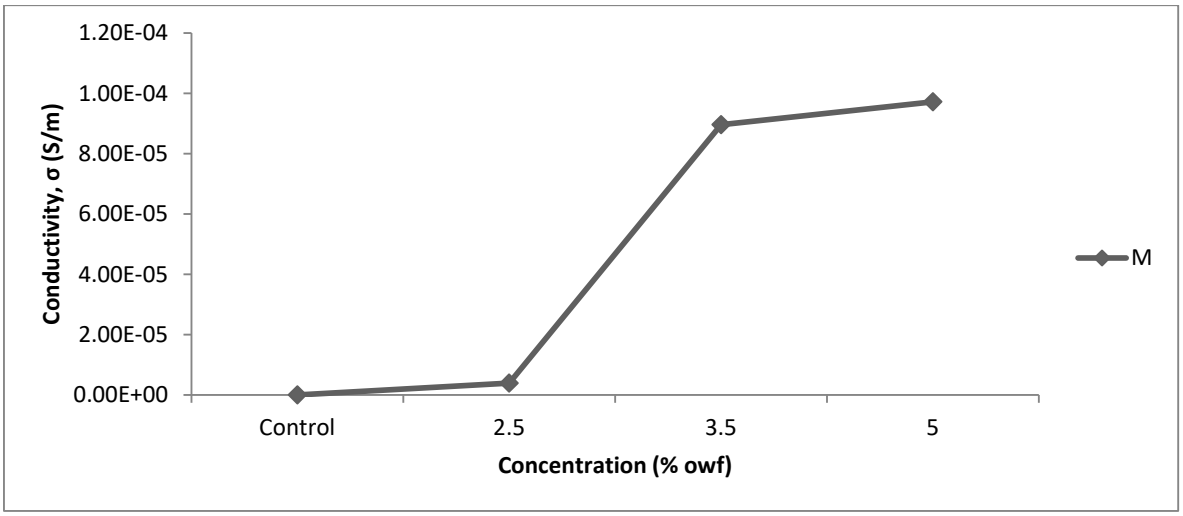

Fig. 4: Conductivity, σ, as a function of concentration (% owf).

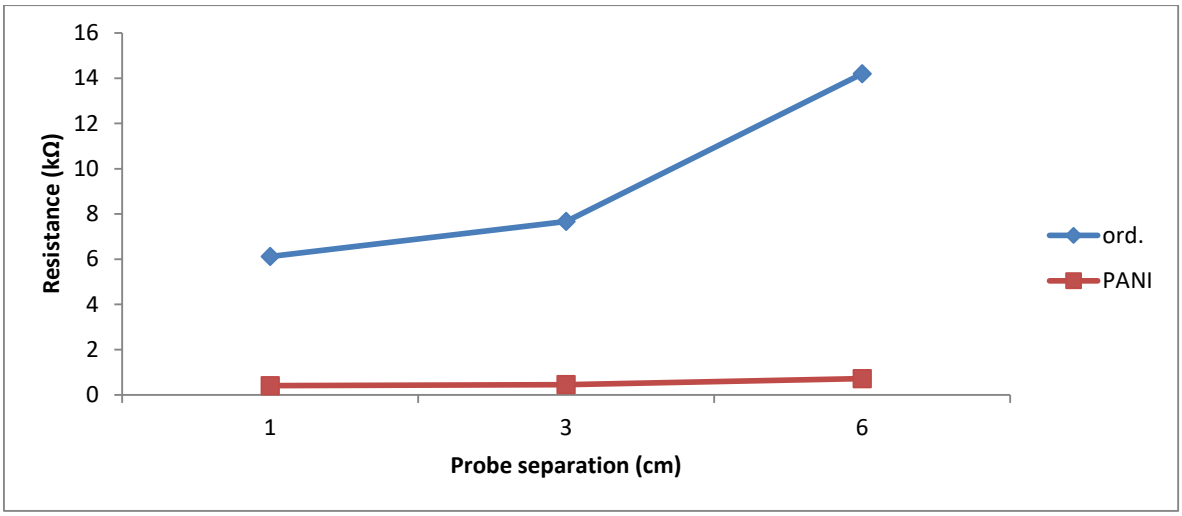

Fig. 5 : Comparison of electrical resistance for 3.5 % untreated (ord.) and PANI treated fabrics.

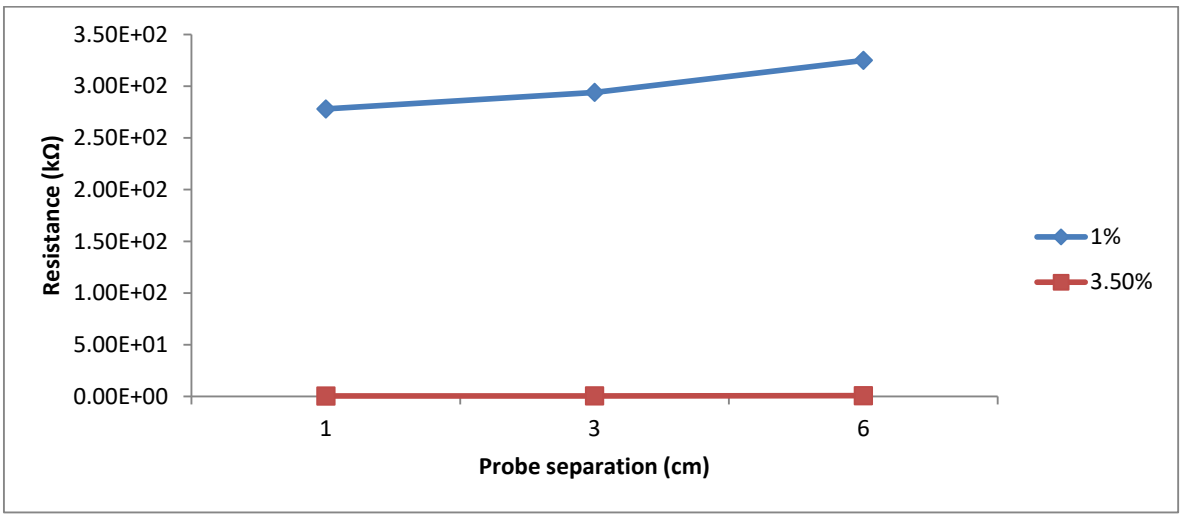

Fig. 6 : Comparison of the electrical resistance of 1% and 3.5% PANI-treated CNT-dyed fabrics.

After polymerization of aniline, the percolation threshold was reduced from 1.0 - 2.5% owf to 0.5 - 1.0% owf. Polymerization of Aniline (to produce PANI, which is an intrinsically conductive polymer, ICP) in the CNT-dyed fabric significantly improved the electrical conductivity of the fabric by more than 14 orders of magnitude between the treated and the untreated of the same % shade (Fig. 5). Comparing when aniline was polymerized in fabrics dyed with 1.0% and 3.5% CNTs, the difference in conductivities was more than 680 orders of magnituden (Fig. 6).

The electrical conductivity here is as a result of a combination of two conduction mechanisms: the cationic 'holes' created along the polyaniline polymer chain backbone allow solitons or electrons to flow freely along the backbone when an electric potential is applied (MacDiarmid, 1993), as well as the network of conductive pathways generated by the CNTs when adjacent tubes are in contact (Grossiord *et al*., 2008), in addition to tunneling or hopping.

Polymerizing aniline on the fabric actually coated the CNTs, thus, holding them in place and improving the fastness characteristics. If more than one polymerization cycle (representing a single coating) is given to the fabric, more conducting polymer is deposited on the fabric, resulting in the generation of more charge carriers and therefore higher electrical conductivity (Neelakandan *et al.*, 2009).

Tensile characteristics

The Figs. 1 – 4 show the results obtained for average breaking force, % elongation, strain at break and work of rupture against concentration. Although all these characteristics vary significantly between the warp and weft directions, the differences are not so much between increasing concentrations.

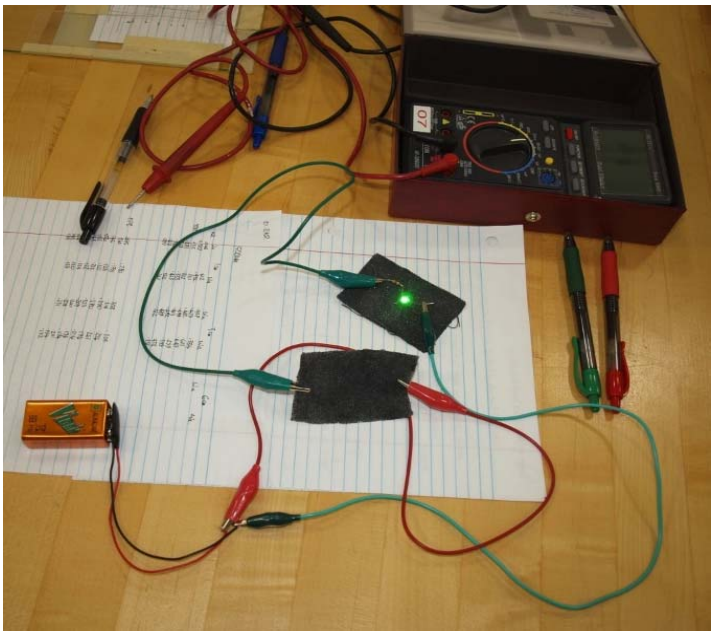

Fig. 7: Photograph of a demonstration in which the CNT-dyed, PANI-treaed fabric is part of a circuit wired to light a LED bulb

A CNT is simply a sheet of graphene rolled into a seamless cylinder. In graphene, each carbon atom is covalently bonded to 3 other surrounding carbon atoms. Graphene layers stacked upon each other constitute graphite. Layered on each other that way, they possess a special ability to slide upon each other, and that explains why graphite is used as pencil-tip materials and in high temperature tribology.

When applied to the fabric, their presence both within and around individual filaments gives the equivalent of applying a lubricant between the filaments. In this way, when a load is applied at the two extremes of a fabric piece, the filaments tend to first straighten out, then untwist, then slide against each other as they attempt to resist stress-bearing (Iliya, 1989); all these are in the presence of the lubricant; they then extend according to their natural extensibilities within the constraints of the type of yarn construction and weave, before finally succumbing to the stress in breakage or failure.

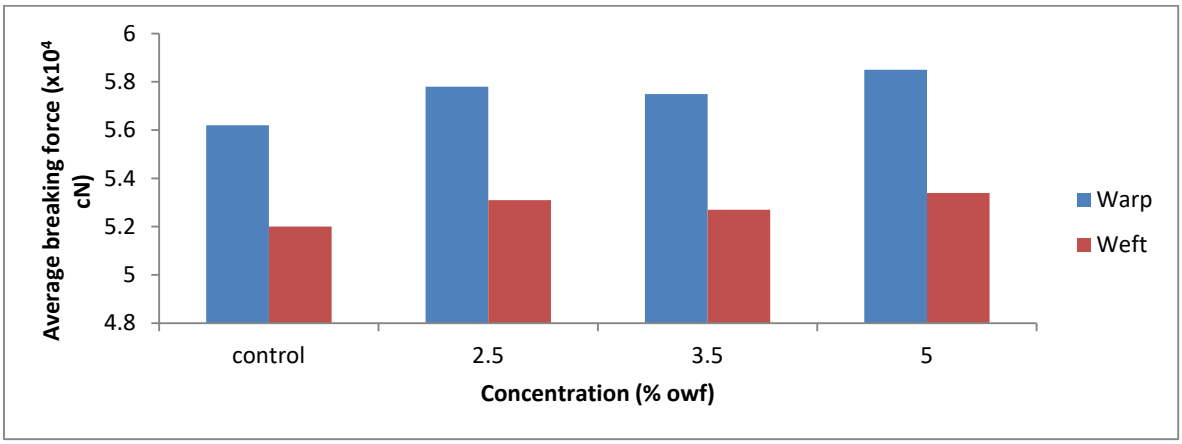

Fig. 1: Average breaking force as a function of concentration

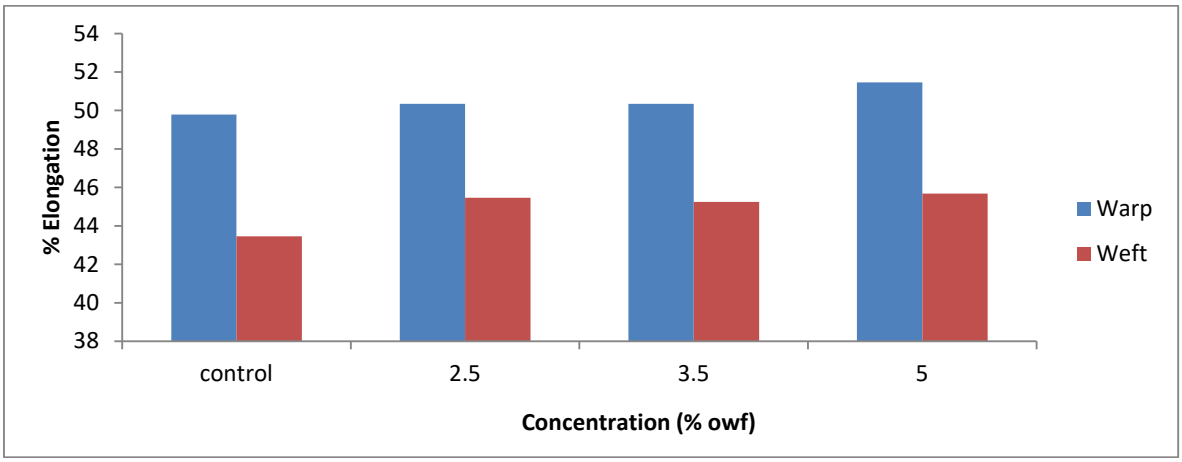

Fig. 2: Percent elongation versus concentration

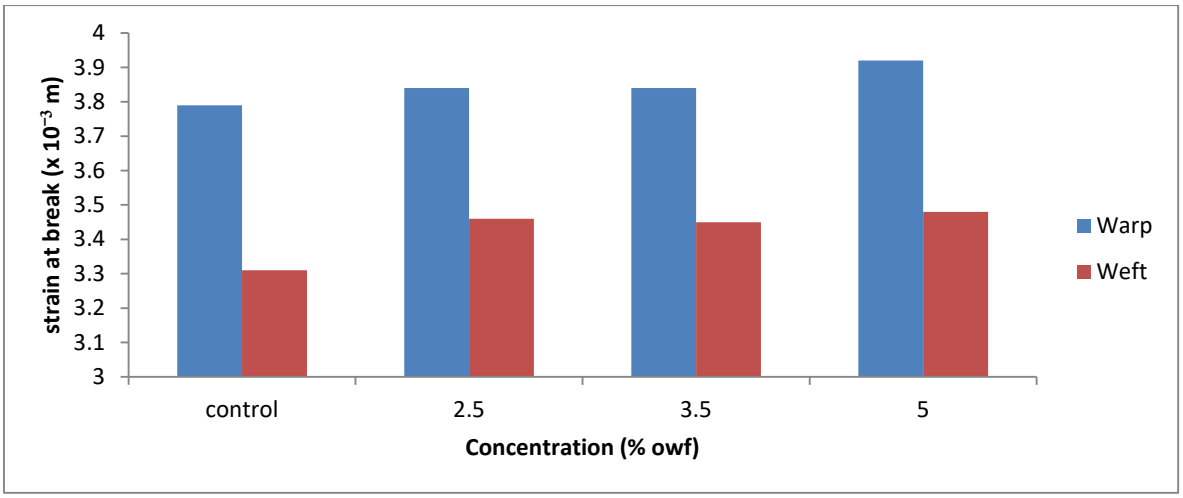

Fig. 3: Strain at break versus concentration

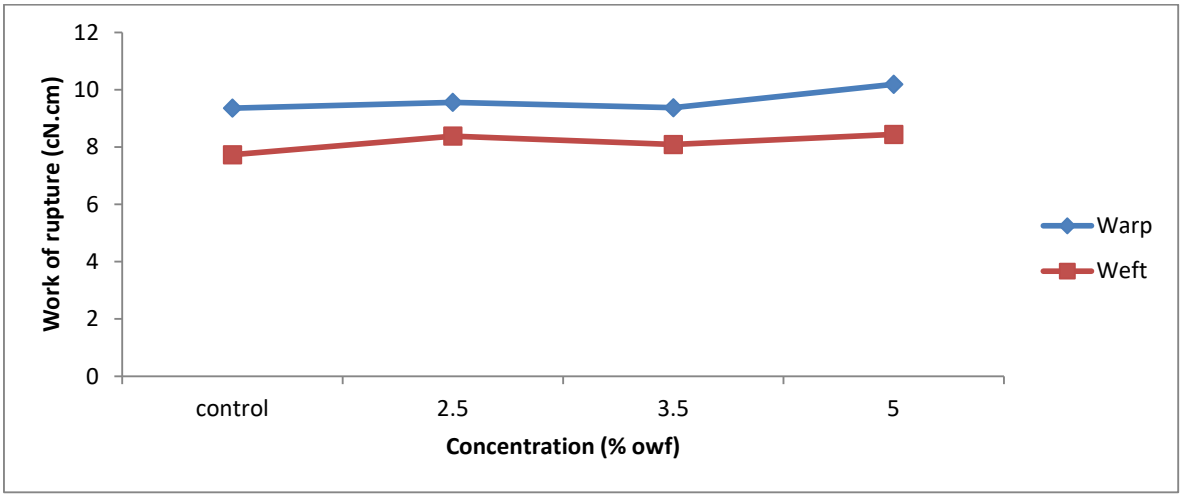

Fig. 4: Work of rupture as a function of concentration of CNTs

This explains why there was an increase in average breaking force, % elongation, tenacity and work of rupture.

Abrasion characteristics

Table 1 summarizes averages of initial and final weights of the samples tested, % weight loss after abrading, the number of rubs and the change in shade assessed by using the AATCC grey scales. There was a decrease in the % weight loss with increase in concentration of CNTs. This is attributed to the lubricating action of the CNTs, so that abradant-fabric wear reduces as the concentration of CNTs increases. This seems to be confirmed by the number of rubs required to rupture some of the yarns. They increased from 86,000 for the control to over 120,000 at 2.5 %. The change in shade was very slight, just as the staining of the abradant material, as evaluated by using the grey scales. This is a further confirmation that a proportion of the CNTs actually penetrated the fibres.

Table 1: Abrasion characteristics

Properties	Control	1% (owf)	2.5% (owf)	3.5% (owf)
Initial weight (g)	0.2144	0.2325	0.2312	0.2178
Final weight (g)	0.1733	0.1952	0.1982	0.2068
Weight loss (%)	19.1697	16.0430	14.2733	5.0505
Number of rubs	86,000	98,000	>120,000	>120,000
Change in shade	5	4	4	3
Staining	5	4	4	3

Conclusion

Results from tests on the functionalized fabric indicated, a sharp drop in resistivity between 1 % and 2.5 %. This region highlighted the percolation threshold. It is 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.

After polymerization of aniline, the percolation threshold was reduced from 1.0 - 2.5% owf to 0.5 - 1.0% owf. Polymerization of Aniline (to produce PANI, which is an intrinsically conductive polymer, ICP), in the CNT-dyed fabric significantly improved the electrical conductivity of the fabric by more than 14 orders of magnitude between the treated and the untreated of the same % shade (Fig. 5). Comparing when aniline was polymerized in fabrics dyed with 1.0% and 3.5% CNTs, the difference in conductivities was more than 680 orders of magnitude (Fig. 6). The aniline seemed to have polymerized on the fabric surface as a spongy layer on the filament surfaces and appears to have sealed the CNTs in place, sandwiched between the PANI layer and the filament surfaces. Polymerization has thus further improved the fastness of the PET/CNT bond by more or less sealing the nanotubes on the fibres.

The fabric thus processed, can be used for electromagnetic interference (EMI) shielding, static dissipation, flexible transistors and electrodes, smart or e-textiles, electric resistance heating systems in homes and furnishings (Battisti, 2009), electrostatic discharge (ESD) protection systems, actuators, chemical and biological sensors, integrated energy storage devices, acid/base chemical vapor sensors, supercapacitors and electrochromics.

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