FUNCTIONALIZED AND PIGMENTED MULTI-WALLED CARBON NANOTUBES FOR AESTHETIC AND STRUCTURAL PROSTHETIC APPLICATIONS

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ABSTRACT

This study synthesised and characterised pigmented multi-walled carbon nanotubes (pMWCNTs) using kaolin from Kogi State, Nigeria, as a sustainable resource for prosthetic reinforcement. The multi-walled carbon nanotubes (MWCNTs) were synthesized via catalytic chemical vapour deposition (CVD) using Fe-Ni supported on kaolin as the catalyst, and functionalized with sulphuric acid (H_2SO_4) and nitric acid (HNO_3) in a 3:1 ratio to enhance dispersion in polymer. Subsequently, the MWCNTs were coated with red and yellow oxide to improve aesthetic. Thermogravimetric analysis (TGA) showed a 3.14% residue at 500 °C. HRSEM imaging showed good dispersion of the nanotubes, and EDX confirmed the presence of 10.4 wt. % Fe (iron) and 5.6 wt. % O (oxygen), indicating successful pigment integration and stability. These results suggest that pMWCNTs can serve effectively as reinforcement materials with potential in visually appealing prosthetic limb applications.

KEYWORDS: Composite, Multi-walled carbon nanotubes (MWCNTs), Pigmented multi-walled carbon nanotubes (pMWCNTs), Prosthetic, Red oxide (RO), Reinforcement, Yellow oxide (YO)

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1. INTRODUCTION

Prosthetic devices play a crucial role in improving the quality of life for individuals with limb loss. Yet, a balance between mechanical performance, wearability, and poseability is hard to achieve (Abubakre *et al.*, 2023; Amsan *et al.*, 2019; Farrar *et al.*, 2023; Medupin *et al.*, 2019). According to the Standards for Prosthetics and Orthotics (2017) of the World Health Organisation (WHO), over 30 million people across the globe are concerned with prosthetics. Prosthetics that otherwise could be durable, flexible, affordable, and dignified confront users with serious barriers in low-resource settings like Sub-Saharan Africa (Farrar *et al.*, 2023; Marino *et al.*, 2015). These conventional prosthetic materials usually fail to meet these requirements, thus posing problems to both functionality and confidence of the user (Abubakre *et al.*, 2023; Alluhydan *et al.*, 2023; Chiriac & Nitu, 2022; Medupin *et al.*, 2020). This project, therefore, investigates pigmented multi-walled carbon nanotubes (pMWCNTs) as potential reinforcement materials. With their superior mechanical and thermal properties, multi-walled carbon nanotubes (MWCNTs) are candidates for high-performance prostheses (Manikkavel *et al.*, 2024; Medupin *et al.*, 2019, 2020; Norazlina *et al.*, 2019). This work is therefore an extension of the studies carried forth by Medupin *et al.* (2019), wherein pigmentation is introduced for further dispersion as well as aesthetic functionality of MWCNTs. In so doing, kaolin obtained from Kogi State, Nigeria, is utilized, thereby tapping somatic local resources and reducing dependence on imported materials, fostering economic and environmental sustainability.

2. MATERIALS AND METHODS

2.1 Materials, Equipment/Apparatus

The lists of equipment and apparatus used in this study are provided in Table 2.1, while the lists of chemicals/reagents in this study are provided in table 2.2 with their percentage purity and suppliers.

Table 1: List of Equipment/Apparatus

Instruments	Model	Manufacturer	Location/Source
Thermostat Oven	Gallenkamp	Gallenkamp, UK	Chemistry Lab, FUT MINNA
Hotplatewith magnetic Stirrer	78HW-1	Gallenkamp, UK	STEP B, FUT MINNA
Sieves (150 µm)	ASTM No. 100	Interlabs, Seithi	Geology Lab, FUT MINNA
Centrifuge	-	Gallenkamp, England	STEP B FUT, MINNA
Catalytic vapour depositor	XD 1200NT	VACUTEC,South Africa	STEP B FUT, MINNA
High resolution scanning electron microscope	Zeiss Auriga	England	Department of Physics, University of the Western Cape
Thermogravimeter	TG 209 F3	Netzsch (Selb, Germany)	Themba Laboratory Cape Town, South-Africa

Table 2: List of Chemicals/Reagents used

Reagent/Chemical Name	Molecular Formular	% Purity	Supplier
Tetraoxosulphate (VI) acid	H_2SO_4	99	BDH
Trioxo nitrate (V) acid	HNO_3	99	BDH
Nickel (II) nitrate hexahydrate	$Ni(NO_3)_2.6H_2O$	99	Sigma-Aldrich
Iron (III) nitrate nonahydrate	$Fe(NO_3)_2\ 9H_2O$	99	Sigma-Aldrich
Acetylene gas	C_2H_2	99	British Oxygen Company, Nigeria
Nitrogen gas	N_2	98	British Oxygen Company, Nigeria
Kaolin	$Al_2Si_2O_5(OH)_4$		British oxygen company Nigeria

2.2 Methods

2.2.1 Preparing Fe-Ni/Kaolin Catalyst

It is a bi-metallic Fe-Ni catalyst prepared by wet impregnation on a kaolin substrate, as explained by Abdulrahaman *et al.* (2017). To begin with, 5 wt. % Ni salt nickel (II) nitrate hexahydrate ($Ni(NO_3)_2•6H_2O$) and 5 wt.% Fe salt iron (III) nitrate nonahydrate ($Fe(NO_3)_3•9H_2O$), thus making 10 wt. % of the catalyst, were dissolved in 50 mL distilled water. The resulting aqueous solution was added drop-wise to 10 g of kaolin, which was used as catalyst support. The slurry formed was then stirred for 1 hour to make it homogeneous, dried at 120°C for 6 hours, calcined at 550°C for 16 hours, ground, sieved by means of a 15 µm mesh, and re-calcined at 500°C for 12 hours, thus ensuring the complete removal of residual nitrates and improving surface properties.

2.2.2 Synthesis of MWCNTs

The method used for the synthesis of MWCNTs was catalytic CVD as outlined by Medupin *et al.* (2019). One gram of the Fe–Ni/kaolin catalyst, spread out evenly in a quartz boat (60 × 25 × 20 mm), was placed at the centre of a horizontal quartz tubular reactor inside an electrical tube furnace. The reactor was first purged with argon at 30 mL/min for 55 minutes, being brought to temperature from room temperature over this period. At 750 °C, the reactor was fed with acetylene (C_2H_2) at 100 mL/min and while the flow of argon was increased to 200 mL/min for 45 minutes, to allow the growth of MWCNTs. After growth, the acetylene flow was stopped, and the argon flow decreased to 30 mL/min for 30 minutes, thereby cooling the reactor down to room temperature under an inert atmosphere. The synthesised MWCNTs were then collected for further processing.

2.2.3 Functionalization of Synthesized MWCNTs

Functionalization of MWCNTs is enhanced for compatibility with polymer matrices using the grafting route of -OH and -COOH functional groups. We oxidized 500 mg with a 3:1 mixture of H2SO4 and HNO3, ultrasonic for 30 min, dilute, filtrated, and washed until neutral, dried overnight at 120 °C.

2.2.4 Optimal Pigmentation Process

The process used for ideal pigmentation is mixing 0.5 grams of functionalized MWCNTs with 20 cm^3 of red oxide (RO) and 6 cm^3 of yellow oxide (YO), stirring for 40 minutes at a pace of 500 rpm, and letting the product dry at 120°C for 12 hours. The ground material was set up for analysis and study.

2.3 Characterization

The characterization of pMWCNTs included different analytical methods. For viewing surface details, High-Resolution Scanning Electron Microscopy (HRSEM), was employed at 5 keV, and Energy-Dispersive X-ray

Spectroscopy (EDX), was set at 20 keV for looking at the elements involved. A thermo gravimetric analysis (TGA) was done using a Netzsch TG 209 F3 Tarsus. Nitrogen atmosphere, with a heating rate of 10°C per minute, was used to analyse the thermal stability of the samples ranging from 35°C to 600°C.

3. RESULTS AND DISCUSSION

This section reports the results of characterisation of unpigmented and pigmented MWCNTs by determination of their morphological and thermal properties.

3.1 HRSEM and EDX, unpigmented and pigmented MWCNT analysis

HRSEM and EDX were utilized in assessing the surface structure, elemental composition, and dispersion quality of the MWCNTs prior to and following pigmentation as indicated in Figure 1.

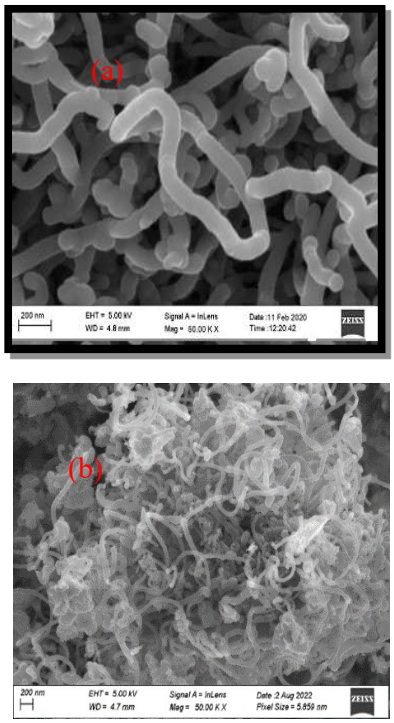

Figure 1: (a) HRSEM of unpigmented MWCNTs (b) EDX of pigmented MWCNTs.

In Figure 1(a), HRSEM images revealed significant differences in morphology between unpigmented and pigmented MWCNTs. Smooth surfaces and strong agglomeration were observed on the unpigmented MWCNTs because of the strong van der Waals forces among them. The accumulation of the particles leads to networks that may troublesome for spreading materials uniformly inside composite matrices as stated by Qazi *et al.* (2021). It was found by Qazi *et al.* (2021) in their studies that pristine MWCNTs tend to gather, thus lowering the effectiveness of the composites. A more spread-out appearance was noted for the MWCNTs after being pigmented in HRSEM pictures. Being attached to the nanotubes, the pigment particles act as gaps, which help lessen the attractive forces and decrease the rate of agglomeration. With this morphology, fillers are now distributed better in the plastic material, which may result in stronger and hotter plastics. Sharma *et al.* (2024) reported that making modifications to MWCNTs surface, enables better distribution of fillers and positively affects the performance of the composite.

To go with the morphology, EDX spectroscopy measured the chemical content of the materials. The results of EDX on unpigmented MWCNTs can be seen in Figure 1 and reveal a C (carbon) peak that indicates they are highly pure. Analysis based on numbers indicates that 100% of the unpigmented MWCNTs are carbon, which shows they are chemically comprehensive.

When comparing, the EDX results for pigmented MWCNTs prove that iron (Fe) and oxygen (O) from the pigments have successfully been introduced, and the surfaced materials are identified as Fe_2O_3 and Fe_3O_4. Pigmented MWCNTs were found to have 10.4 wt% iron, and 5.6 wt% oxygen, meaning the pigment is attached

without harming the tube's structure. On the other hand, the uncoloured MWCNTs were up to 98% carbon pure, while the coloured variants contained extra 12–15% of other elements, which further proves the effectiveness of the functionalization process (Shamsazar *et al.*, 2024) Also, the detection of Fe and O in the EDX analysis means iron oxide functional groups have been applied successfully to the MWCNTs during pigmentation. As a result of the modification, the nanotubes chemistry changes and they become more compatible with the polymer. Through these modifications, the mechanical and thermal properties of the composite are enhanced due to the fact that the filler and the matrix adhere better. Dubey *et al.* (2021) describe that the functionalization of certain chemical groups on carbon nanotubes enables them to disperse and strongly bond with other materials in a composite. It is found by studying employing functionalized CNTs that they are able to handle tasks such as, water purification, drug delivery, and advanced composite materials better, pointing to the significance of making necessary surface changes.

HRSEM and EDX show that the pigmentation process changes the structure and make-up of MWCNTs. The changes improve how the polymers are distributed and also increase how well the atoms bond at the polymer-nanotube boundaries without harming the nanotubes' structure.

3.2 Tga Of Unpigmented And Pigmented Mwcnts

The thermogram curve in Figure 2 provides insight into the thermal stability of the unpigmented MWCNT and the pMWCNT. Key thermal parameters such as the Initial Decomposition Temperature ($T_{initial}$), Onset Decomposition Temperature (T_{onset}), Maximum Decomposition Temperature (T_{50}), Degradation Temperature Range (ΔT), Residue at 500 ^{0}C, and Final Residue temperature (T_{final}), were analysed to evaluate the material performance under thermal stress, (as shown in Table 3).

For the black MWCNT in Figure 2, $T_{initial}$ of approximately 580°C was more thermally stable than the optimized pMWCNT whose degradation began at a significantly lower temperature of ~270°C. For black MWCNT, the starting T_{Onset} was 599.22°C, which was significantly higher than the 284.11°C for optimized pMWCNT. At T_{50}, i.e., 50% decomposition of the material weight, black MWCNT reached ~630°C, while optimized pMWCNT reached ~400°C, indicating a faster rate of mass loss in the latter.

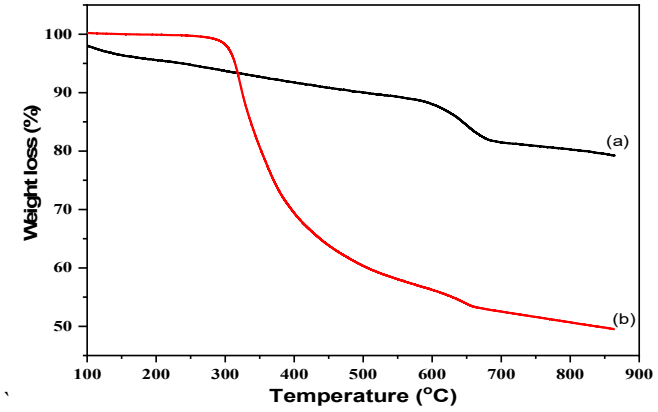

Figure 2: TGA of black MWCNT and optimized pMWCNT

Table 3: TGA of black MWCNTs and optimised pMWCNTs

Sample	$T_{initial}$ (°C)	T_{Onset} (^{0}C)	T_{50} (°C)	ΔT (°C)	Residue at 500°C (%)	T_{final} (°C)
Black MWCNT (a)	~580	599.22	~630	599.22–677.11	11.76	~677
pMWCNT (b)	~270	284.11	~400	284.11–555.27	3.14	~555

The ΔT of black MWCNT was also narrower, from 599.22–677.11°C, corresponding to a quicker decomposition process. Optimized pMWCNT decomposed in a broader temperature window of 284.11–555.27°C, corresponding to a slow and controlled decomposition pattern. The 500°C residue of black MWCNT was 11.76%, corresponding to the preservation of the catalytic impurities, whereas optimized pMWCNT had a mere 3.14% residue, corresponding to higher material purity. The T_{final} as approximately 677°C in the case of black MWCNT, whereas the optimal pMWCNT resulted in complete degradation at ~555°C.

These findings are echoed by Neto *et al.* (2023), where it was observed that the incorporation of MWCNTs into natural-fiber-based composites enhanced thermal stability and reduced mass loss. Similarly, in the present study, the pigmented MWCNTs showed progressive and sustained thermal disintegration with 3.14% residue at 500 °C and prior decomposition temperatures compared with un-pigmented MWCNTs. This is indicative of pigments' addition not only changing thermal character but also reducing residual catalyst composition.

In contrast to previous studies such as Medupin *et al.* (2019), where unmodified MWCNTs exhibited inferior dispersion and agglomeration in polymer matrices, pigmented MWCNTs here exhibited enhanced morphological homogeneity, as evidenced through HRSEM. The pigment particles function as dispersing aids and surface spacers that promote nanotube separation as well as interfacial adhesion. These developments are consistent with those of Sharma *et al.* (2024), which established enhanced composite performance using surface-engineered nanotubes. Overall, these developments serve to complement further the promise of pMWCNTs as thermo-mechanically stable, well-dispersed reinforcement fillers for high-demanding applications such as prosthetic limb components. The increased dispersion and surface modification of pMWCNTs directly contribute to the mechanical homogeneity and interfacial bonding in prosthetic composite materials. Addition of pigment not only brings in heat modification but also aesthetics, which are critical in aesthetically acceptable prosthetic limbs. The stability of the shape of the limb is maintained at varied temperatures by controlled thermal degradation, which is highly advantageous in the lower-limb prostheses that are widely used. Therefore, pMWCNTs can be employed extensively in order to prepare enhanced prosthetics in resource-poor areas.

4. CONCLUSION

In this research, the pMWCNTs were successfully synthesised, coated, and characterised. RO and YO shows their capacity as a prospective reinforcing and aesthetic agents in prosthetic limbs. More dispersed, better heat conductive with the help of pigments, and highly compatible with polymer matrices, they are worthy of use in prosthetics for reinforcement and aesthetics. Because the process used locally sourced materials, the process is cost-effective and sustainable, hence it can promote new economic growth where there are few available resources. Further research should then be done to confirm the biocompatibility of pMWCNTs for use in prosthetic implants.

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