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Comparative Study of Multi-walled Carbon Nanotube Reinforced Natural Rubber Nanocomposite and Multiflex Dynamic Response – 2 Artificial Foot

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Abstract-

The desire to restore the quality of life to amputees has been on the front burner in recent years. This study compares the functional properties of a home-grown nanocomposite (NC) and multiflex dynamic response-2 artificial foot (M.DR2). The inherent challenge of ensuring uniform distribution of multi-walled carbon nanotube (MWCNT) in host matrices was addressed by the use of sodium dodecylbenzene sulfonate ($C_{18}H_{29}NaO_3S$). Carbon nanotubes (CNTs) were synthesised via catalytic chemical vapour deposition (CCVD) technique and the NC was produced using an electrically heated hydraulic press. While the initial decomposition temperature (T_{onset}) showed that the newly developed material with 260.01 °C is more thermally stable than M.DR2 artificial foot with the temperature of 238.17 °C, incorporation of MWCNTs into the unfilled NR matrix proved a significant change in T_{onset} . MWCNT loading was found to influence the moisture content of the reinforced matrix by about 7% with the NC being 35% more thermally stable than M. DR2 artificial foot. SEM/EDS micrographs indicated complete embedment of MWCNTs in NR matrix, thereby making it more suitable than M. DR2 foot which was inundated with cavities, thereby making it susceptible to early failure. While it took both materials 120 days to attain saturation point NR/MWCNT-3 is 93% more dimensionally stable than M. DR2 and also demonstrated better resistance to wear. The wear rate results revealed that M. DR2 wears faster than NR/MWCNT-3 by approximately 32%. It can, therefore, be concluded from the foregoing that the home-grown material is to be preferred to its foreign counterpart for anthropomorphic prosthetic foot application.

Key words: NR/MWCNT, TGA/DTG, SEM/EDS, Water Absorption, M. DR2 foot

1. Introduction

The historical twists and turns of prosthetics paralleled the growth of human medicine, culture and civilisation. Right from the dawn of human medicine to date, prostheses have been developed for function, cosmetics and appearance; to provide a psychological sense of wholeness [1]. In the early age of human history, prosthetics began as uncomplicated wooden crutches and leather cups as apparent in some earliest recovered pottery archive [2]. This metamorphosed into modified crutches or pegs to allow for the functionality of the hands.



Although they were considered primitive, earlier prosthetics were very functional and incorporated many vital prosthetic principles upon which today's technological advancements are hinged [3]. The first true rehabilitation aids acknowledged as prostheses were made in Egypt, Greece and Rome [4]. These three great civilizations ushered in the development of scientific approach towards medicine and prosthetic science [5].

Earlier prosthetics were either too heavy or cumbersome and could only be used in battle [2]. There were no considerations for daily functions such as walking and running. They were more cosmetic than functional; only intended to hide the humiliation and dishonor that accompanied defeat in battles [6],[7]. The industrial revolution, however, ushered in prosthetic progression fueled by money available to amputees following the American Civil War [8]. The challenge of returning to normal lifestyle by soldiers who survived World War II but rendered limb deficient became obvious to all. And so, with the growing number of amputees and increased consciousness, the development of functional prostheses became inevitable. The users were much more mobile and relatively independent with the use of such devices, even though they were, by no means, comfortable to wear [9]. From such heavy, bulky, immobile limbs to light, more functional limbs, prosthetics have evolved. Currently in use are modern materials such as plastics, carbon fibres; strong but lightweight metals like titanium and aluminium, which are water resistant and better able to withstand harsh environmental conditions [10]. Other suitable and effective candidate materials are polymeric composites which have emerged with much lower cost but better flexibility for use in third world countries [11].

The full potential of CNT/polymer NC as an emerging technology remains to be fully harnessed. A few challenges still exist that require quick attentions in order to appreciate the wide range of applications of this advanced material. These include preparation of controllable CNTs with high purity and reproducibly high performance, breaking up entangled CNTs and dispersing them homogeneously in a polymer matrix as well as improving the stress transfer from the matrix to CNTs reinforcement [12]. Obviously the ultimate mechanical and other functional properties of CNT/polymer nanocomposites (NCs) are determined by the inherent properties of CNTs [13]. Therefore adequate attention needs to be paid to all the activities of CNTs growth if CNT/polymer NCs of high quality will be developed.

The growing demand for prosthetic limbs in third world countries is attributed to the increasing rate of amputation resulting from lack of access to basic secondary healthcare and its astronomical price, where it is available. The situation is worsened today in Nigeria. With the activities of insurgents and unabated communal clashes, many people have been rendered limbless and require urgent help to have their lives back. A recent report from victims of insurgency had it that thousands of amputees in the North-Eastern Nigeria remain hopeless as a result of the loss of their limbs and inability to afford the cost of foreign prostheses [14]. An amputee's need for initial prosthetic limb goes beyond an immediate replacement but multiple replacement limbs and repairs are often unavoidable over a lifetime. These call for the use of materials that are more durable and able withstand the harsh weather in African countries. According to a white paper by McGimpsey and Bradford [7], a prosthetic replacement is needed typically every 6 – 12 months of use for an amputee whose bones are still growing, and an adult

amputee will, on average, use about 15 – 20 artificial limbs during his/her lifetime. This is essentially because a replacement is required every 3 – 5 years for adults [10],[15].

However, while it appears there are a growing number of people with limb loss in low-income countries around the world, very little is being done to solve the problem of lack of trained personnel in these countries. Reports by the World Health Organisation (WHO) show that while the current supply of skilled technicians needed for prosthetic services falls short by 40,000, it will take up to 50 years to train just 18,000 skilled professionals [16]. Another daunting challenge is that of importing components to build prosthetic limbs. This will not only attract more cost but may also fail earlier because they may be designed for very different lifestyle and climatic conditions.

Therefore, because majority of the amputees in the third world countries are low income farmers, herdsman and nomads who rely on physical labour for survival, the traumatic condition of losing a limb has a negative consequence on their physical ability and appearance; it causes profound psychological damage and eventual economic incapacitation. It is against this background that this study is being undertaken to contribute to efforts geared towards solving the problem of availability of home-grown artificial foot by developing a prosthetic foot that will compete favourably with its foreign counterparts, from locally available materials.

2. Methodology

2.1 Material Processing (If needed)

Dynamic response-2 artificial foot was supplied by the Orthopaedic Workshop of the Leprosy Mission, Minna, Nigeria and the natural rubber used for the production was supplied by Alhson Laboratory Equipment Consult, Zaria, Nigeria. Multi-walled carbon nanotube (MWCNT) was synthesised using VACUTEC Chemical Vapour Deposition equipment (model: XD-1200NT, USA) at the Centre for Genetic Engineering and Biotechnology, Federal University of Technology, Minna, Nigeria. Stearic acid, sulphur, zinc oxide (ZnO), 2-2-dithiobis benzothiazole (MBTS), and 2,2,4-Trimethyl-1,2-dihydroquinoline polymer (TMQ) were received from the Nigeria Institute of Leather Science and Technology, Zaria, Nigeria while sodium dodecylbenzene sulfonate ($C_{18}H_{29}NaO_3S$), nickel (II) nitrate hexahydrate, $Ni(NO_3)_2 \cdot 6H_2O$, iron (III) nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$ and aluminium oxide, Al_2O_3 were supplied by Sigma-Aldrich with percentage purity in the range of 95.0 – 99.9% .

2.2 MWCNT Synthesis and Purification

The growth of multi-walled CNTs took place in a cylindrical fixed tube reactor, VACUTEC CVD equipment (XD-1200NT, South Africa), of length 1010 mm and internal and external diameters of 52 mm and 60 mm respectively. In these conditions, 1.0 g of Fe-Ni supported by Al_2O_3 was spread evenly on a (60 by 25 by 20) mm dimension quartz boat and placed at the centre of the reactor while still at room temperature. Argon was then fluxed at 30 mL/min for 55 minutes, as the furnace temperature was raised from ambient to 750 °C prior to the growth, in order to purge the system of any trapped air. Acetylene was then fluxed at 100 mL/min with immediate increment in the flow rate of argon to 200 mL/min for the reaction time of 45 minutes. At the expiration of the reaction time, the flow rate of argon was returned to 30 mL/min and acetylene flow was stopped. This condition was sustained for 30 minutes after which the reactor was cooled to room temperature. The cylinder, at the end of the growth, was opened to collect the MWCNTs for purification and functionalisation.

About 10 mg of MWCNT was added to 4 mL HNO₃ 30% in a beaker. This was then placed in the ultrasonic cleaner with temperature set to 45 °C and run for 180 minutes. After ultrasonication was complete, the suspension was washed repeatedly in distilled water until neutral pH was achieved. The MWCNTs were then dried in the furnace for 12 hours at 70 °C. The MWCNTs were also treated with sodium dodecylbenzene sulfonate, (C₁₈H₂₉NaO₃S) in order that homogeneous dispersion of the filler can be achieved in the matrix. A solution of 1.2 mM C₁₈H₂₉NaO₃S in 50 cm³ distilled water was prepared in the laboratory and 20 mg MWCNTs was added and ultrasonicated for 30 minutes at ambient temperature. The MWCNTs were afterward filtered, washed thoroughly and dried again for 12 hours at 70 °C.

2.3 Preparation of Natural Rubber Nanocomposites

Natural rubber compounds were prepared at 65±2 °C temperature in an open two-roll mixing mill (5183, USA). The rotor speeds for the front and rear rolls were adjusted to 30 rpm and 18 rpm respectively. The formulations used for preparing the rubber NCs are given in Table 1. Mixing was performed according to ASTM D-3182 on the two-roll mill with working distance of 300 mm and outside diameters of 115 mm and gear ratio of 1.

Table 1: Formulation of NR/MWCNTs Composite

Ingredient	NR/MWCNT-0 (g)	NR/MWCNT-3 (g)
NR	100.0	100.0
ZnO	5.0	5.0
Stearic Acid	2.0	2.0
TMQ ^a	1.0	1.0
MWCNT	0.0	3.0
MBTS ^b	1.0	1.0
Sulphur	2.5	2.5
Total	111.5	114.5

where

a: 2,2,4-Trimethyl- 1,2-dihydroquinoline polymer

b: 2-2-dithiobis (benzothiazole)

Zinc oxide (ZnO), stearic acid and TMQ were first mixed with masticated NR, followed by the incorporation of MWCNTs. While ZnO and stearic acid served to activate the vulcanisation process, TMQ served as an antioxidant. Vulcanisation ingredients, MBTS and sulphur were then added towards the end of mixing process with MBTS coming first to accelerate the process.

Table 2: Mixing Procedure of NR/MWCNTs on Two-Roll Mill

Mixing order	Mixing time (minutes)
NR	4.0
ZnO, Stearic acid, TMQ	3.0
MWCNT	5.0
MBTS	1.5
Sulphur	1.5

Total time (minutes)	15.0
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The parameters of the mixing process for the two-roll mill are presented in Table 2. After compounding, the compounds were left for 24 hours to allow for full interaction of the ingredients. They were then cured at a temperature of 150 ± 2 °C and pressure of 0.2 MPa for 10 minutes in an electrically heated hydraulic press. The test samples were subsequently cooled under pressure at ambient conditions and neatly packed for characterisation.

2.4 Thermo-gravimetric Analysis

Thermal decomposition was observed in terms of global mass loss by using Perkin Elmer TGA 4000 with model number N520-0110. About 25 mg of the sample was spread on a 7.4 mm diameter open sample pan and 4.2 mm deep. The apparatus detects the mass loss with a resolution of 0.1% as a function of temperature. The temperature change was controlled from 30 °C to 950 °C at a heating rate of 10 °C/min. The sampling segment was set as 0.5 second per point.

Before the commencement of the run, the purge gas, nitrogen, was run through the furnace at 50 ml/min for 30 minutes to establish an inert environment in order to prevent any unwanted oxidative decomposition. The TG and DTG curves that were obtained from TGA run were analysed by using universal analysis 2000 software from TA instruments.

2.5 Scanning Electron Microscopy and Energy Dispersion Spectroscopy

Nanocomposite of mass 0.05 mg was spread on a sample holder coated with carbon adhesive tape and sputter coated with Au-Pd using Quorum T150T for 5 minutes prior to the analysis. The sputter coated samples were characterised using Zeiss Auriga high resolution scanning electron microscopy (HRSEM). The microscope was operated with electron high tension (EHT) of 5 kV for imaging.

X-rays were captured at an angle of 35° for 300 seconds with Au-Pd using Quorum T150T. A tad size of roughly 10 to 20 mm, free from dirt and other debris, was isolated for compositional analysis. The sputter coated samples were characterised using Zeiss Auriga HRSEM. The microscope was operated with electron high tension (EHT) of 20 kV for EDS and then the elemental composition of the sample was determined.

2.6 Water Absorption Test

Water absorption analysis was undertaken according to ASTM D-7031-04 standard. Five specimens were dried in an oven at 70 °C for 6 hours. These dried specimens were afterwards placed in distilled water and kept at room temperature according to a method adopted by Mohebbi *et al* [17]. Wet weights of the samples immersed in water were determined within the soaking period of 6 months at room temperature. The weights were determined to a precision of 0.001 g using an analytical weighing balance every 30 days. Water absorption as well its rate was determined according to the following equations.

$$MC_t = (M_t - M_o) / M_o \times 100 \quad (1)$$

where MC_t is water absorption at time t (%), M_t is wet weight at time t (g) and M_o is the dried weight (g).

$$\text{Rate}(\%/hr) = \Delta X/\Delta t = (X_{t_i} - X_{t_{i-1}})/(t_i - t_{i-1}) \quad (2)$$

where $\text{Rate}(\%/hr)$, X_{t_i} and $X_{t_{i-1}}$ are absorption in immersed condition at time t_i and t_{i-1} .

2.7 Wear Rate Test

In accordance to ASTM G65 standard, abrasion wear test was conducted using TR-50 Dry Abrasion Tester. The specimens (M. DR2 and NR/MWCNT-3) were firmly held in the holder and normal load was applied to them with the face of the specimens in contact with a rotating rubber wheel. The test specimens were pressed against the rotating wheel at a specified force of 5 N using a lever arm while a restricted flow of grit abraded the surface of the test specimens. The wheel rotated in such a way that the contact faces move in the direction of the sand flow. Weight loss of test samples indicated that wear has taken place. Materials of higher abrasion resistance will have a lower volume loss.

Weight loss was calculated using Equation 3.

$$\Delta W = W_1 - W_2 \quad (3)$$

where ΔW is weight loss of the specimen, W_1 and W_2 are weights of the specimens before test and after test respectively.

Volume losses of the specimens were computed using Equation 4.

$$\Delta V = \Delta W/\rho \times 1000 \quad (4)$$

where ρ is the experimental density of the specimen. This is determined by gently placing the specimen in a beaker of water while noting the volume change as a result of the weight of the specimen.

The specific wear rates of the specimens were calculated using Equation 5.

$$W_s = \Delta V/(F_n \times S_s) \quad (5)$$

where W_s is the wear rate of the specimen, F_n is the normal load applied of the specimen and S_s is the sliding distance through which the specimens were traversed. The equations are adopted from the works of Agarwal *et al* [18] and Vemuri and Vincent [19].

3. Results and Discussion

3.1 Carbon Nanotube Synthesis

Figure 1 represents the morphologies of the unpurified and purified CNTs using HRTEM. The geometry of the synthesised CNTs shows that they are MWCNTs. The thickness of the wall represents multiple of rolled layers of graphite. Metallic impurities in the form of amorphous carbon and metal carbide which may have remained during thermal catalysis process were precipitated by HNO_3 used in the purification. A reduction was noticed in both the length and diameter of the purified MWCNTs which can be attributed to the removal of crystalline impurities in the as-produced CNTs. The results are also indicative of a long-tube growth of the purified (25.86 μm) and as-produced (36.11 μm) CNTs with 1250 aspect ratio. It can therefore be concluded that alumina support and incipient wetness impregnation method are appropriate

for the synthesis of CNTs as reinforcing filler in natural rubber matrix for prosthetic foot application.

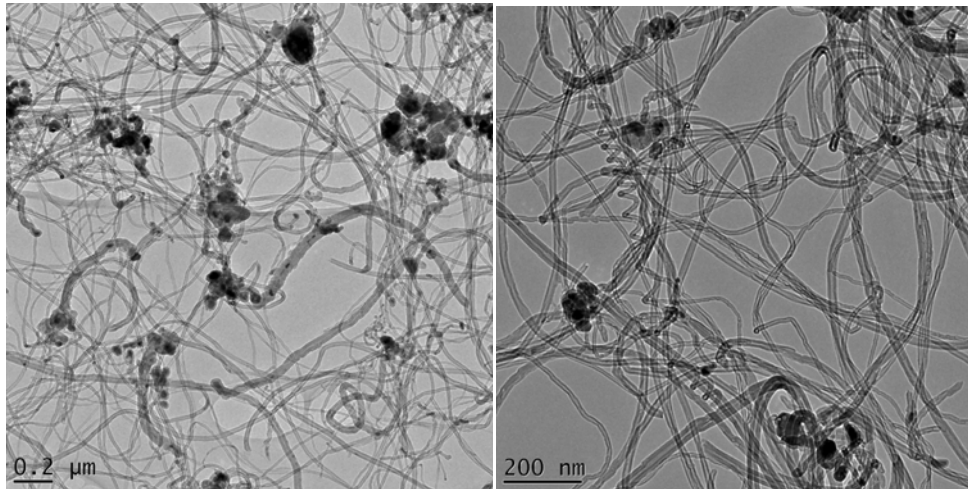


Figure 1: HRTEM images of as-produced (left) and purified (right) MWCNTs

3.2 Thermo-gravimetric Analysis

The thermal stability of M. DR2 and the unfilled as well as the filled rubber vulcanisate was investigated using TGA/DTG as illustrated in the thermographs shown in Figures 2, 3 and 4. A list of the major events from the thermographs is presented in Table 3. Noticeably, the initial decomposition temperature (T_{onset}) which is an indication of thermal stability of the materials was higher in the newly developed NC (260.01 °C) as compared to M. DR2 which was 238.17 °C and the unfilled matrix (255.12 °C). The inclusion of the filler, MWCNTs, shows a significant change in the T_{onset} of the NC [20]. The improvement of the onset temperature is attributed to the combined effect of nano-confinement and barrier effect of the incorporated nanofillers [21],[22]. The degradation profile of the NR and the resulting NCs lends credence to the fact that the unfilled matrix is less thermally stable than the NCs. And even without the filler, the unfilled NR shows greater stability when compared to M. DR2. The temperature range within which complete degradation of the materials take place lie between 250 °C and 600 °C. Beyond this range, weights had been stabilised.

The first set of temperature peaks on the DTG curves corresponds to the initial removal of moisture and all other volatiles from the samples before the commencement of degradation. The temperature profile as seen in Table 3 shows that about half of the heat required to completely eliminate moisture from the unfilled NR was needed to dehydrate NR/MWCNT-3. In the same vein, a third inflection point which showed up after T_p might also have resulted from the combined effect of nano-confinement and barrier effect of the incorporated nanofillers. Earlier researchers may have been cautiously silent about this because of limited explanations for such a phenomenon in the literature. The moisture content of the material was noticed to increase with MWCNTs loading by about 7%. But when compared to the moisture content of M. DR2 which is 4.25%, NR/MWCNT-3 is about 35% more thermally stable than the existing prosthetic foot.

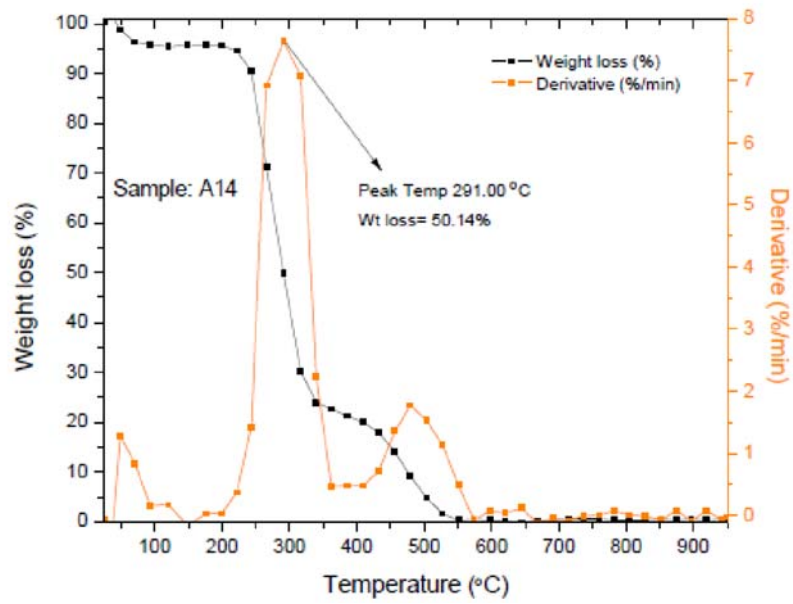


Figure 2: TGA/DTG Thermographs of Dynamic Response – 2 artificial foot

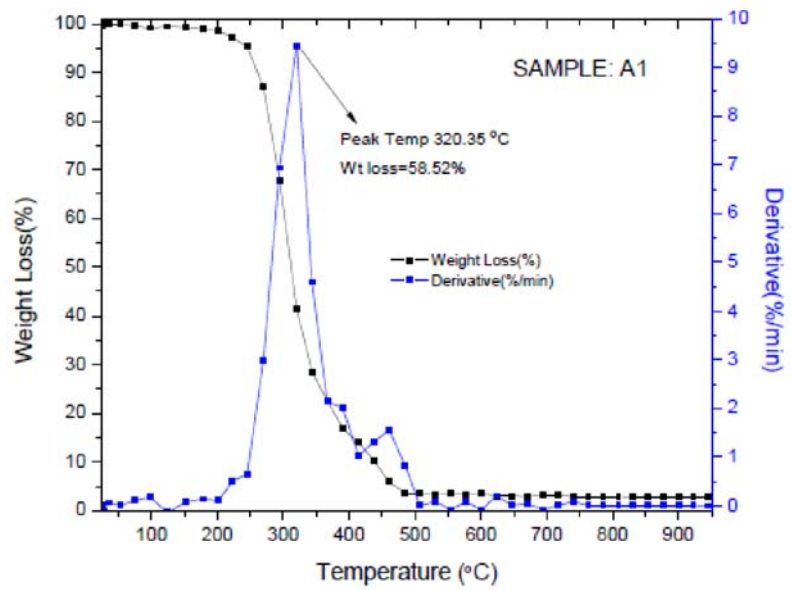


Figure 3: TGA/DTG Thermographs of NR/MWCNT-0 nanocomposite

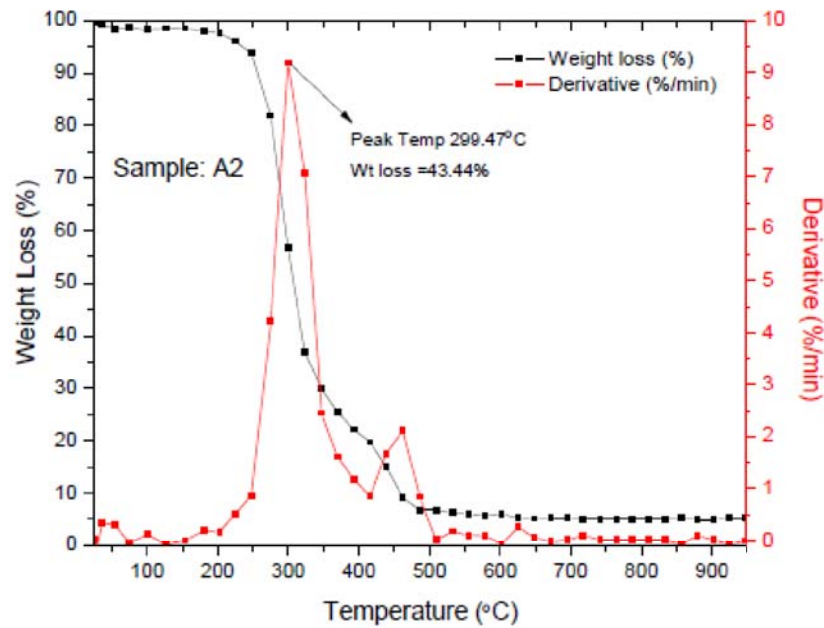


Figure 4: TGA/DTG Thermographs of NR/MWCNT-3 nanocomposite

Table 3: Thermal Parameters of M. DR2 and NC Samples from TGA and DTG Thermographs

Serial No	Samples Code	T_p (°C)	T_{50} (°C)	T_{onset} (°C)	Degrad. Temp. (°C)	Residue (%)
1	M. DR2	291	292.24	238.17	201.85-363.61 363.61-552.32	0.83
2	NR/MWCNT-0	320.35	310.91	255.12	202.40-623.06	2.86
3	NR/MWCNT-3	299.47	307.77	260.01	202.18-416.72 416.72-648.02	5.46

3.3 SEM/EDS Analysis

The images and spectra shown in Figures 5 and 6 are those of NR/MWCNT-3 and M. DR2 artificial foot. It is obvious from the SEM micrographs that the filler phase were completely embedded in the matrix phase. This is made possible by good interfacial interaction between filler and matrix in agreement with and earlier work by Mittal [23] and Osman *et al* [24]. Figure 6 appears to be inundated with cavities which make it more susceptible to early failure under dynamic loads and weathering, in comparison to NR/MWCNT-3 produced [25]. EDS analysis was utilised to identify the elements on and under the surfaces of the test samples. There may have been false elements identification as a result of some unavoidable errors resulting from unsolicited inclusions from sample preparation. While some elements in the samples were not detected by the X-ray, some elements which were not in the composition of the samples were identified. This may also be due equipment errors.

Compositional analysis of the NC confirms the presence of the elements listed as part of the vulcanisation ingredients; MWCNTs surface treatment chemicals as well as filler elements themselves. The purification and complete functionalisation of the fillers accounts for the strong adhesive force at the interface of the two major phases which prevents filler pull-out during the

fracture of the test samples in readiness for SEM/EDS analysis [26]. Investigating the elemental analysis presented in the SEM micrographs and EDS spectra, it can be pointed out that apart from the main elements suspected to have emanated from the major constituents of the NCs, other trace elements also appeared which could have come about as a result of the activities and materials used for catalyst and CNT synthesis and test sample preparation. Different peaks such as carbon (C), zinc (Zn), sodium (Na), sulphur (S), oxygen (O) and traces of calcium (Ca), gold (Au), silicon (Si) and potassium (K) are quite noticeable in the spectra. The figures ascertain the peaks as the existing elements of the NCs analysed with C and O being the major elements; O, S, Zn and Na being the minor elements and K, Al, Na, Si and Ca as the traces. This is in harmony with a study conducted by Dale [27] and Dale [28] on the range of concentration by weight that make up major, minor or trace elements in a composite ($C > 10 \text{ wt}\%$ = major; $C > 1-10 \text{ wt}\%$ = minor ; $C = 1 \text{ wt}\%$).

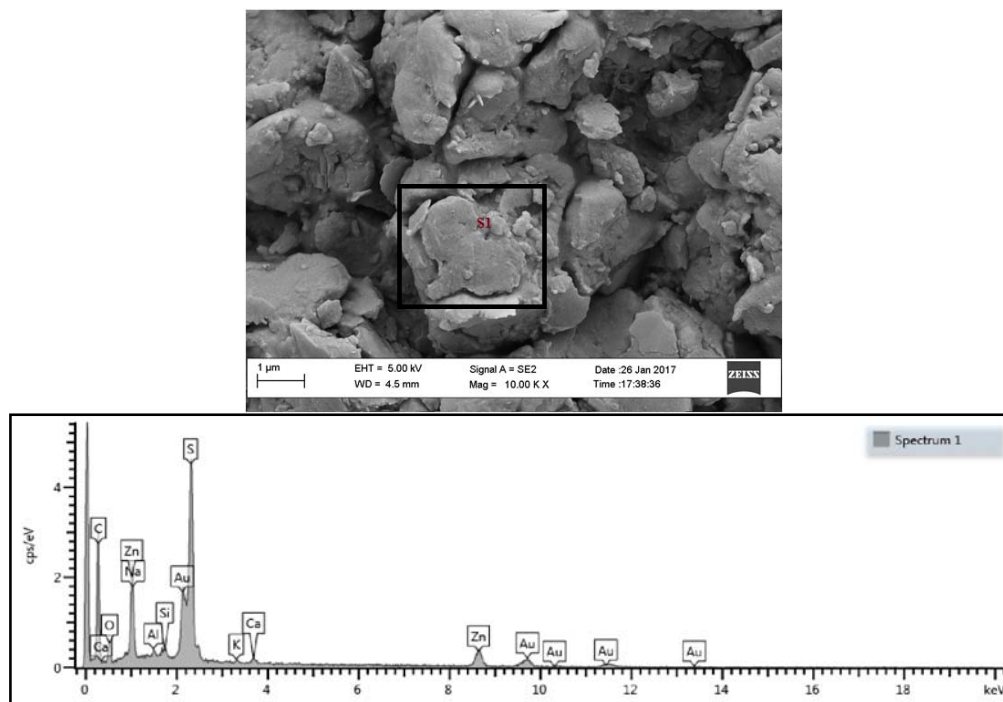


Figure 5: SEM microgram (top) and EDS spectrum (bottom) of NR/MWCNT-3 Nanocomposite

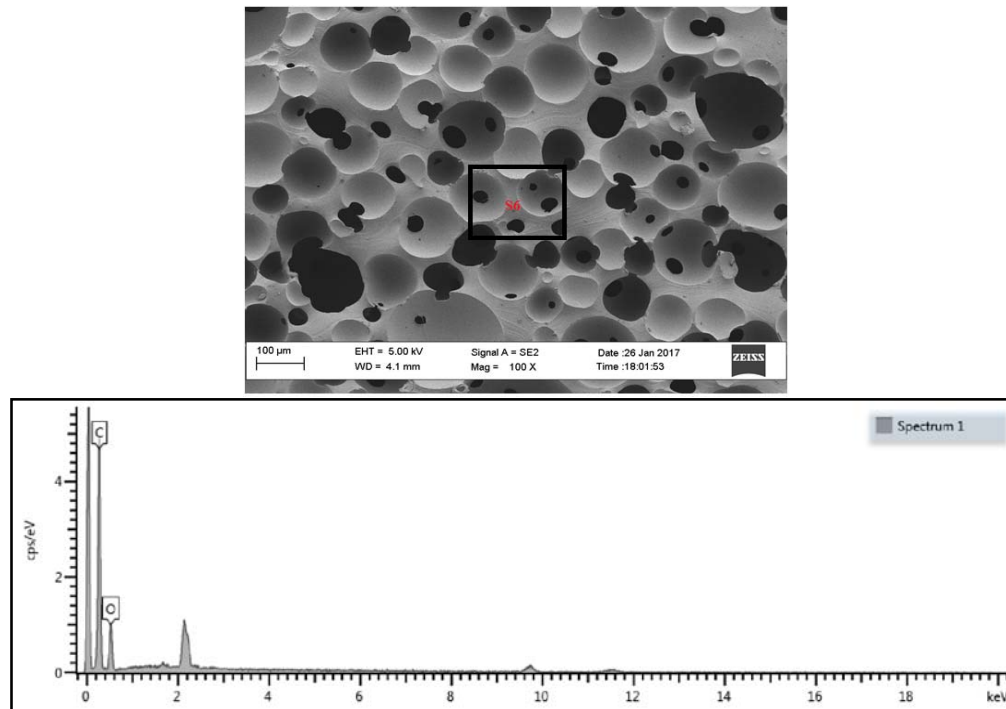


Figure 6: SEM microgram (top) and EDS spectrum (bottom) of FAF Test Specimen

3.4 Water Absorption Analysis

In order to further demonstrate the superiority of the locally made prosthetic material over M. DR2, water uptake tests were carried out as the knowledge of the rate of water absorption of materials is key to the understanding of the microbiological activities going on in them and their stability in humid environment. The first 60 days of soaking M. DR2 in water witnessed the faster rate of water uptake while NR/MWCNT-3 experienced steady uptake in its first 30 days of full immersion in distilled water. However, the rate continued to reduce afterwards until it stabilised after 120 days when the materials must have reached their saturation point [29].

By the end of the first 30 days, M. DR2 has gained about 1% of its weight while NR/MWCNT-3 which has the least value of water absorption has only gained approximately 0.1% of its entire weight. This indicates that the fillers in the NC were completely embedded in the matrix (Figure 5). This is occasioned by good filler wetness [30] brought about by the surface treatment given to the filler materials. It can therefore be concluded that the locally made prosthetic material possesses better stability parameters when compared to the foreign materials analysed alongside. Also, because of the lower water uptake and its rate, microbiological activities are less supported by NR/MWCNT-3.

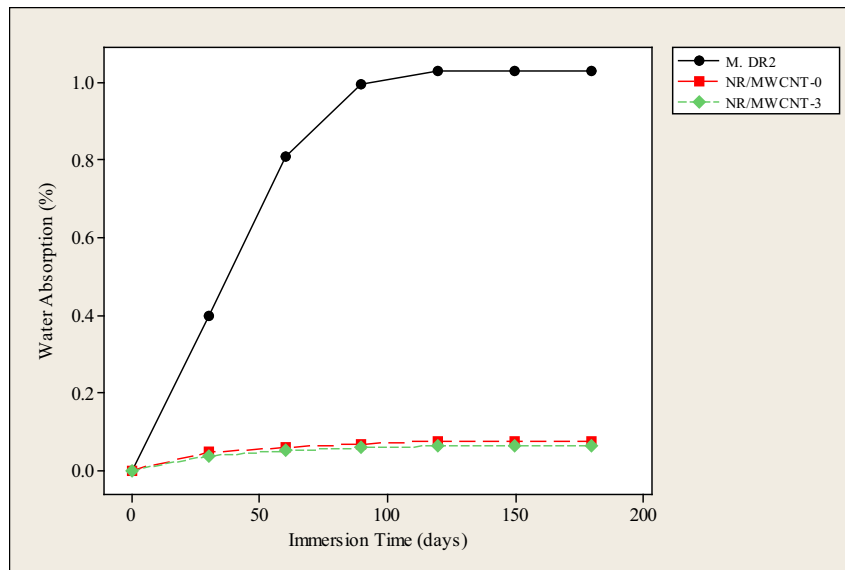


Figure 7: Variation in Water Uptake with Immersion Time for Unfilled Vulcanisate, MWCNT-3 and M. DR2 at Room Temperature

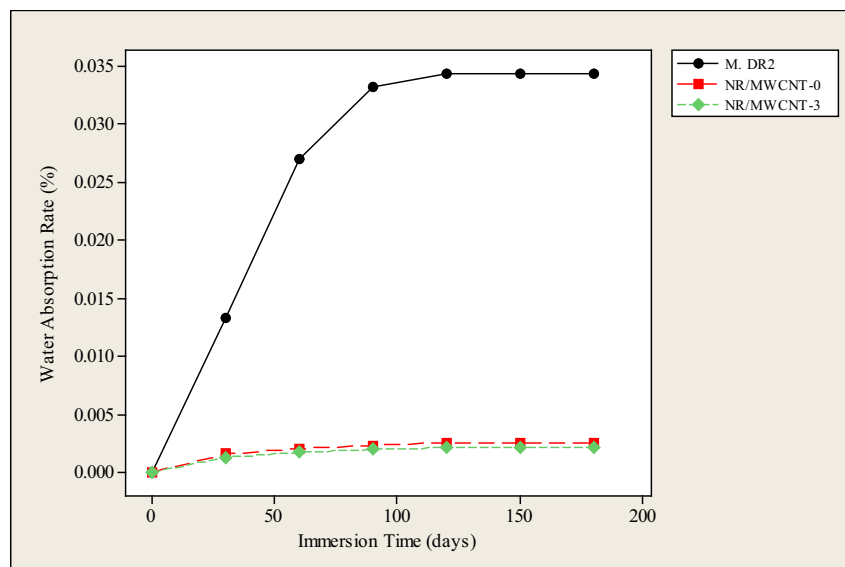


Figure 8: Water Absorption Rate for Unfilled Vulcanisate, MWCNT-3 and M. DR2

3.5 Wear Rate Results

Wear resistance test of NR/MWCNT-3 and M. DR2 was carried out. The decision to single out these two materials was consequent upon the former's unique and superior properties over the unfilled material for prosthetic foot application. The results are presented in Table 4.

Table 4: Wear Rate Results

Sample	Initial Mass (g)	Final Mass (g)	Density (g/cm ³)	Vol. Loss (cm ³)	Sliding Dist. (m)	Wear Rate (cm ³ /Nm)
NR/MWCNT-3	3.577	3.561	0.36	0.016	4.45	0.001977
M. DR2	3.107	3.089	0.31	0.018	4.01	0.002896

Table 4 shows that NR/MWCNT-3 has a lower volume loss when compared to M. DR2. It can, therefore, be concluded that NR/MWCNT-3 offers better options in wear resistance since materials of higher abrasion resistance are reported to have a lower volume loss according to Agarwal *et al.* (2013). By implication, more of the M. DR2 than the newly developed novel material (NR/MWCNT-3) would be required by an adult amputee in a life time. Hence, a lot more than what poor amputees in rural and middle income countries like Nigeria can afford is expended preferring the M. DR2 to the newly developed anthropomorphic prosthetic foot, as a result of earlier failure of the former.

4. Conclusion

This study compares the water absorption capacity, thermal stability, wear resistance and morphological properties of M. DR2 material to NR/MWCNT-3 material for anthropomorphic prosthetic foot application. MWCNT was produced using chemical vapour deposition technique with Fe-Ni bimetallic catalyst supported on alumina. The dual actions of HNO₃ and C₁₈H₂₉NaO₃S for MWCNT treatment enhanced its interfacial interaction as well as homogeneous distribution in the matrix; hence resulting improved functional properties. The new material is about 93% more dimensionally stable, 35% more thermally stable and 32% better resistant to wear than M. DR2. This improved functional properties of the newly developed material is traceable to its better morphology when compared to the cavity infested M. DR2. It can therefore be concluded that the locally made NR/MWCNT nanocomposite is better suited as a material for prosthetic foot application in sub-Saharan Africa as it demonstrates superior properties with the different tests carried out in the study. The future of this work centres on improving its aesthetic acceptability among users by finding the appropriate colouring agent that will not impact negatively of the inherent properties of the filler material.

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