New Insights in Decoration of Carbon Nanotube for Improved Electrical Conductivity and Thermomechanical Properties of Polymer Nanocomposites

V.S. Aigbodion, P.A. Ozor N.I. Sukdeo
Africa Centre of Excellence, ACE-SPED University of Nigeria Nsukka Nigeria
Department of Metallurgical and Materials Engineering, University of Nigeria, Nsukka, Nigeria
Faculty of Engineering and Built Environment, University of Johannesburg, South Africa
[4]Department of Mechanical Engineering, University of Nigeria, Nsukka, Nigeria
victor.aigbodion@unn.edu.ng, pozor@uj.ac.za, nsukdeo@uj.ac.za

Abstract

Carbon nanotubes (CNT) are promising materials due to their outstanding mechanical and electrical properties. However, the electrical percolation threshold obtained in epoxy/carbon nanotube (CNT) nanocomposites is one of the lowest among conductive nanocomposites. There exist research efforts to improve the electrical percolation threshold of epoxy/CNT with the addition of silver nanoparticles. The aim of this novel work is to use biosynthesized silver nanoparticles (GAg.NPs) as a replacement for high-cost Ag.NPs for the enhancement of the electrical properties of epoxy/CNT. The nanocomposites were produced by using 0.1, 0.2, 0.3, 0.4 and 0.5% CNTs and 0.5% GAg.NPs in the epoxy matrix. The morphology, electrical conductivity and thermomechanical properties of the developed composites were determined. The results show an increment in the electrical conductivity and storage modulus of the epoxy/CNT with the addition of GAg.NPs. The work established that the addition of GAg.NPs to epoxy-CNT can be used to improve electrical conductivity and storage modulus of epoxy-CNT composites for electronic applications.

Keywords
Carbon nanotube, Silver nanoparticles, Epoxy, Electrical and Thermomechanical properties

1. Introduction

Electrically conductive polymer materials have been proven to be used in fuel cells like printed circuit boards, electronic devices, anti-static electricity, electromagnetic shielding, etc (Backes et al., 2017; Md Saleh et al., 2020). However, there are little numbers of inherently conductive polymers commercially available in the market today (Jin and Park, 2013). Research and development have over the years tried to develop conductive polymer by the addition of conductive reinforcement to the non-conductive polymer. The conductive fillers such as graphite, carbon fibers, carbon black, metal fibers, metal powder, carbon nanotubes (CNTs), etc have been used successfully in the production of the conductive polymer (Rudawska 2020; Hao et al.; 2021; Ma et al. 2014). In all the mentioned conductive fillers, CNTs exhibits fascinating usage in the production of the conductive polymer (Ma et al., 2014).

Carbon nanotubes (CNTs) are normally produced from concentrically-rolled graphene sheets that have asymmetric helicity (Backes et al., 2017). The SP^2 of the carbon atoms of the CNTs provide high thermal conductivity as well as excellent high electronic and chemical stability (Md Saleh et al., 2020). Carbon nanotubes (CNTs) are one of the conductive materials used in the production of electrically conductive polymer for the electronic industry because CNTs possess good electrical conductivity, a large aspect ratio, low mass density and appreciable thermal properties (Jin and Park, 2013). However, dispersion of CNTs in polymer have been reported to precipitate agglomeration due to strong Van der Waals forces (Rudawska, 2020). This can result in reduction of the electrical and mechanical properties. Hybridization of CNTs using inorganic materials helps to enhance the electrical and mechanical properties of the composites. The use of low-cost inorganic reinforcement can lower the high cost of CNTs usually used in the manufacturing of conductive polymer. Silver inorganic particle is usually used to enhance the better dispersion of CNTs in the production of conductive polymer for the electrical and electronic industries (Hao et al.,

2021). The silver acts as a transport medium to CNTs and enhances better dispersion. Ma et al. (2014) reported improved electrical conductivity when Ag nanoparticle are decorated with carbon nanotube for epoxy composites. The decoration of CNTs using Ag enhanced uniform dispersion of CNTs in polymer matrix, although the cost of silver does not justify continuous usage of Ag in CNTs. Hence, there is urgent need to synthesize Ag nanoparticles from local sources to ameliorate the prohibitive cost and achieve sustainability This work will report the decoration of CNTs using biosynthesize Ag nanoparticles.

2. Materials and Method

The CNTs with 10-20µm length and the average size of 10-40nm was purchased in China (Hongwu International group of company), see Figure 1. The high peak of carbon obtained in EDS in Figure 1 shows the high purity of CNTs used in the research.

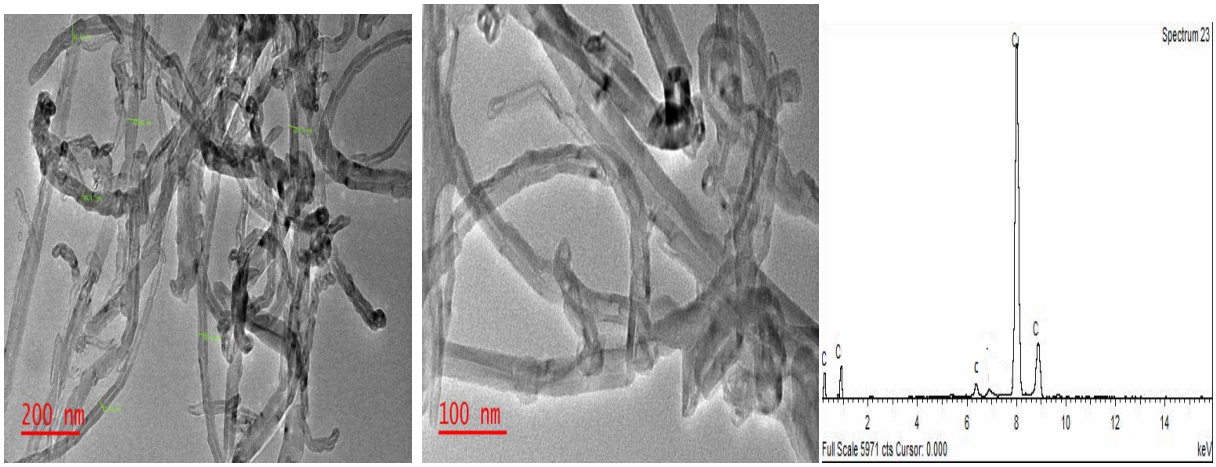

Figure 1. TEM/EDS image of CNTs

The GAg.NPs were synthesized using Cashew leaves. The fresh Cashew leaves used in this work were gotten around the environment of the University of Nigeria Nsukka Nigeria. The fresh leaves were washed with distilled water and dried. 100ml of ethanol was then added to the washed Cashew leaves and left for 1hr, after then a solution of $AgNO_3$ (100ml) was added. The addition of $AgNO_3$ to the Cashew leaf extract samples produced an instant colour change from an original yellow solution to a dark brown solution, see Figure 2. The reaction was left for 30min before heating in an electric oven at 100^{o}C under stirring at a speed of 2000rpm. After heating the solution, there was centrifugation for 1hr to obtain the solid Ag-NPs (Mudasir et al., 2016). Figure 2 display the TEM image of the GAg.NPs. Spherical and round image of GAg.NPs are visible in Figure 2. The average size obtained for the GAg.NPs was 45-65nm. The high peak of Ag in the EDS spectrum shows that high purity GAg.NPs was obtained.

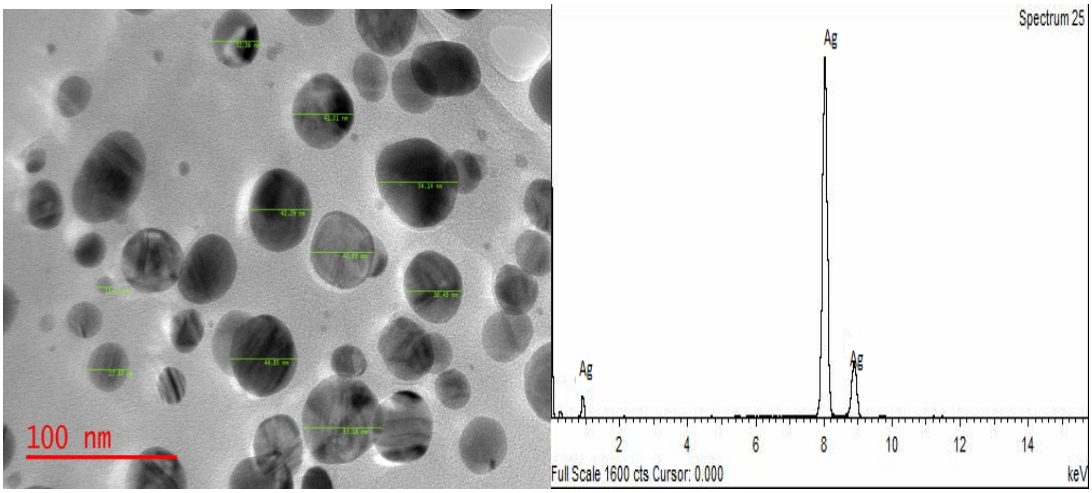

Figure 2. TEM/EDS image of AgNPs

It is worthy of note that LY556 (HERENBA BRAND) epoxy with density 1.15-120g/cm^3 and HY951 Hardener with density 0.98 g/cm^3 were used in this research. Before decoration of CNTs with GAg.NPs, the CNTs were modified by treating with 100ml of 30%H_2O_2 and 65%HNO_3. The functionized CNTs were mixed GAg.NPs using sonicator Sonics ultrasonicated model: Vibra-Cell model VC 505 (solid probe) for 60 min at 400 W with optimal addition of 0.5% GAg.NPs was obtained in the formulation. The modified solution stir casting method was used in the development of the novel composites. The white Epoxy resin and Hardener (HY951) were mixed using a ratio of 10:1 and then stirred with a magnetic stirrer for 15 min. The composites were produced using 0.1, 0.2, 0.3, 0.4 and 0.5 with constant 0.5% GAg.NPs. Kaise insulation equipment model SK5010) was used to determine the electrical conductivity of the samples. The test was conducted per ASTM by placing the samples between two electrodes. Equation 1 was used to compute the electrical conductivity

$$\sigma = \frac{1}{\rho} = \frac{d}{(R_p)A} \tag{1}$$

The microstructure of the samples was determined using a scanning electron microscope (SEM) model: VEGA 3 TESCAN. Thermomechamical tests were carried out as per ASTM D4065 standard using DMA machine model: Perkin Elmer 8000

3. Results and Discussion

Figure 3 displayed the results of the electrical conductivity of the conductive polymer. It was observed that the addition of GAg.NPs to CNTs raises the electrical conductivity of the epoxy nanoparticles. The composites with GAg.NPs @CNTs have higher conductivity than the epoxy/CNTs composites. The improvement of the epoxy/GAg.NPs @CNTs can be attributed to the imminence of electric percolation, in which polymer (dielectric) is separated by mini capacitors and leads to increment in electrical conductivity. A 9.1x10-3S/cm and 5.6x10-13S/cm were obtained for epoxy-0.5%CNTs-0.5%GAg-NPs and epoxy matrix. The increment in electrical conductivity is expected since GAg.NPs @CNTs developed conductive network configurations and 3-D dense structures in the epoxy matrix. The conductive paths in the epoxy matrix creates quick mobility of charge carriers in the system. The direct contact of the GAg.NPs @CNTs in the epoxy resulted in ohmic conduction and non-ohmic conduction which results in indirect contact of GAg.NPs @CNTs in the matrix. This work is in par with the work of Smolen et al (2021).

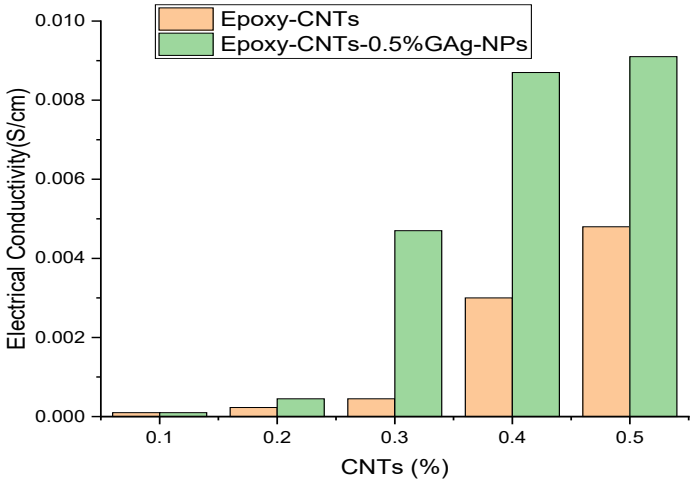

Figure 3. Variation of electrical conductivity with CNTs addition

Figure 4 displayed the DMA results of the nanocomposites. It was seen that the epoxy-0.5%CNTs-0.5%GAg.NPs have a higher storage modulus of all samples under investigation. Addition of 0.5%GAg.NPs to CNTs helps to shift the storage modulus curve to higher temperatures and elevates the glass transition temperature. As per Putz et al (2008), the DMA properties of thermoset materials are influenced by the CNTs by the creation of an interface that is rigid between the CNT and epoxy resin and restricts epoxy chains and also incomplete crosslinking reaction which lead to the formation of epoxy-CNTs interphase. However, greater interphase leads to a greater impact on the mobility of the polymer chains, which resulted in higher thermal stability as observed in Figure 4. It was observed that the composite with GAg.NPs @CNTs has the higher DMA of all the samples under investigation. This was attributed to the formation of strong GAg.NPs @CNTs. The GAg.NPs @CNTs lower the rate of burning and raise the DMA of the composite for an electronic application. A similar observation was obtained in the work of Backes et al. (2017).

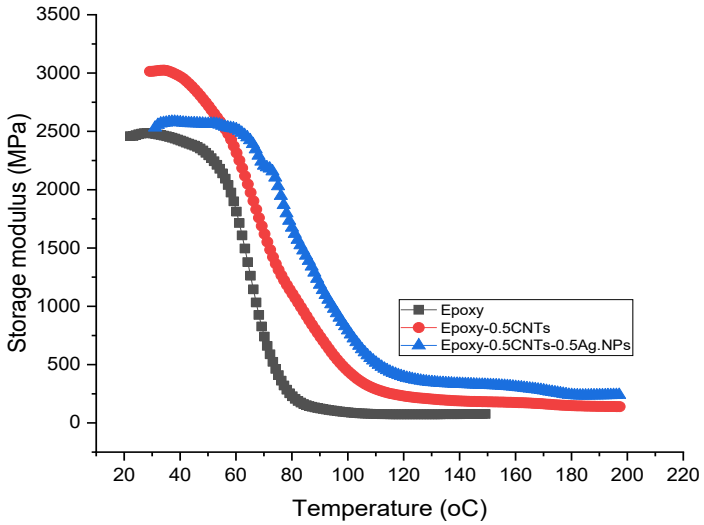

Figure 4. Variation of Storage modulus with Temperature

Figures 5 through Figure 6 present the SEM images of the epoxy and the composites. It is evident that the lamellar structure of the polymer was revealed in Figure 5. There were uniformity in the distribution of CNTs@GAg.NPs, which appears as white phases visible in Figure 6. Defect such as segregation of particles was not observed in the composites. This white phase can explain can account for the observed higher electrical conductivity and storage modulus in the composite. The presence of GAg.NPs @CNTs helps to alter the network multilayer structure of CNTs and enhances good interfacial bonding between the polymer and the reinforcement.

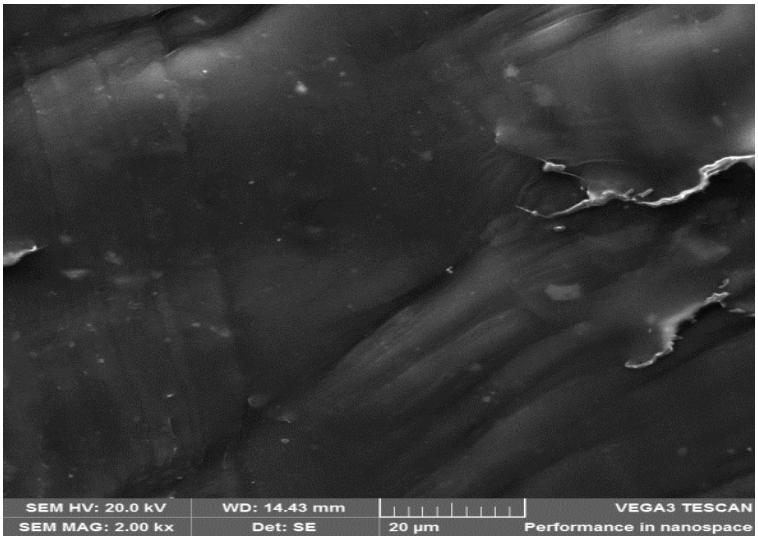

Figure 5. SEM image of epoxy

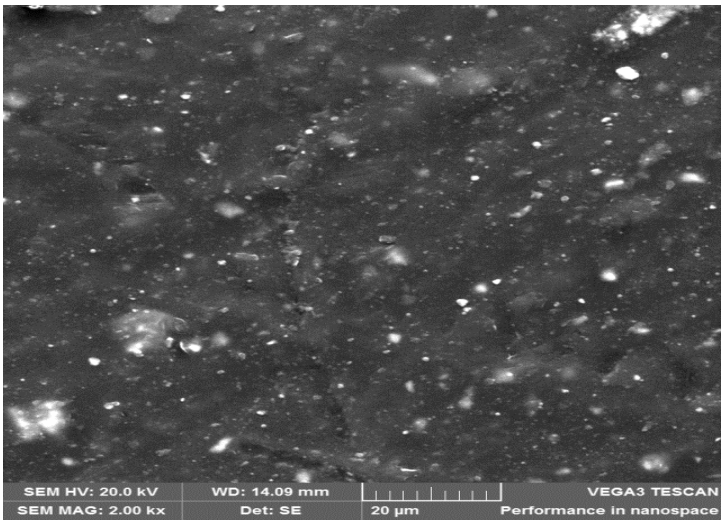

Figure 6. SEM image of epoxy-05CNTs-0.5%GAg.NPs

4. Conclusions

New information was obtained in using biosynthesized silver nanoparticles in the decoration of CNTs for the production of conductive polymer for electronic industries. In the course of the work, the following conclusions can be made:

1. The epoxy-0.5%CNTs-0.5%GAg.NPs composite was successfully produced using the modified solution stir cast method

2. The uniform epoxy-0.5%CNTs-0.5%GAg.NPs and good dispersion of the CNTs can help to raise the electron path and hence increase the electrical conductivity, and storage modulus of the developed composite.
3. Biosynthesized silver nanoparticles can be used for ensuring good dispersion of CNTs for the production of conductive polymer.

References

Backes, E. H., Sene, T. S., Passador, F. R., & Pessan, L. A. Electrical, Thermal, and Mechanical Properties of Epoxy/CNT/Calcium Carbonate Nanocomposites, Materials Research, 21, (1), 2017.

Hao, Y.; Li, Q.; Pang, X.; Gong, B.;Wei, C.; Ren, J. , Synergistic Enhanced Thermal Conductivity and Dielectric Constant of Epoxy Composites with Mesoporous Silica Coated Carbon Nanotube and Boron Nitride, Nanosheet. Materials, 14, 5251, 2021.

Jin, F.-L., & Park, S.-J. , Recent Advances in Carbon-Nanotube-Based Epoxy Composites. Carbon Letters, 14, (1), pp. 1–13, 2013.

Ma, Y., Wu, D., Liu, Y., Li, X., Qiao, H., & Yu, Z.-Z. , Electrically conductive and super-tough polypropylene/carbon nanotube nanocomposites prepared by melt compounding, Composites Part B: Engineering, 56, pp. 384–391, 2014.

Md Saleh, S. S., Suhaimi, S. M., Md Akil, H., & Mohammad, N. F. , Properties of Carbon Nanotubes-Calcium Carbonate Hybrid Filled Epoxy Composites, Materials Science Forum, 1010, pp. 136–141, 2020.

Putz KW, Palmeri MJ, Cohn RB, Effect of crosslink density on interphase creation in polymer nanocomposites. Macromolecules; 41: pp. 6752–6756, 2008.

Rudawska, A., Experimental Study of Mechanical Properties of Epoxy Compounds Modified with Calcium Carbonate and Carbon after Hygrothermal Exposure. Materials, 13, (23), 5439, 2020.

Shakeel Ahmed Saifullah Mudasir, Ahmad Babu, Lal Swami, Saiqa Ikram, Green synthesis of silver nanoparticles using Azadirachta indica aqueous leaf extract, Journal of Radiation Research and Applied Sciences 9, (1), pp. 1-7, 2016.

Smolen, P.; Czujko, T.; Komorek, Z.; Grochala, D.; Rutkowska, A.; Osiewicz-Powezka, M., Mechanical and Electrical Properties of Epoxy Composites Modified by Functionalized Multiwalled Carbon Nanotubes, Materials, 14, 3325, 2021.

Bibliographies

Paul Amaechi Ozor is the West African Sub-Regional Coordinator of Industrial Engineering and Operations Management Society International. He holds a bachelor's degree in Mechanical/Production Engineering from the Enugu State University of Science and Technology as well as Masters and PhD in Industrial Engineering and Management from the University of Nigeria, Nsukka. Dr Ozor had been a Project Manager in a reputable Engineering company in Nigeria for many years. He had been a faculty member of University of Nigeria Nsukka since 2009, and has served the Department of Mechanical Engineering and Faculty of Engineering in various capacities prior to his appointment as the head of Department of Mechanical Engineering in August 2021. Dr Ozor is a Scholar of the Association of Commonwealth Universities (ACU), and a fellow of The World Academy of Science. He is a fellow of the global excellence stature (GES) of the University of Johannesburg. He is currently serving as a Senior Research Associate of the University. As a speaker and participant in international conferences, seminars and workshops, he has visited several countries on research grounds. Dr Ozor has published research articles in many peer reviewed local and international Journals and conference proceedings. He has supervised significant local and international postgraduate students to successful study completion. He is an external examiner to University of the Witwatersrand, South Africa. He is a member of the Nigeria Society of Engineers (NSE) and registered with the Council for the Regulation of Engineering in Nigeria (COREN). His research interest is not limited to Asset Management, Quality, Operations Management, Reliability Engineering, Environmental Influence, Sustainable materials, lean 6 sigma, smart manufacturing e.t.c.

Victor S. Aigbodion is a Professor**,** at the Department of Metallurgical and Materials Engineering, University of Nigeria, Nsukka Nigeria. He is a Visiting Professor, at the Department of Mechanical Engineering, University of Benin, Benin City Nigeria. Visiting Professor, at the Faculty of Engineering and the Built Environment, University of Johannesburg. Professor Extraordinaire, at the faculty of Engineering and Built Environment, Tshwane University of Technology Pretoria South Africa. Visiting Professor, at the Nigerian Institute of Mining and

Geosciences. Industrial Liaison officer to the World Bank Africa Centre of Excellence on Sustainable Power and Energy Development (ACE-SPED). Member of the policy committee, World Bank Africa Centre of Excellence on Sustainable Power and Energy Development (ACE-SPED). Editorial Advisory Board Recent Patents on Nanotechnology, Betham Science publishers. Editorial Board Journal of Metallurgical and Materials Engineering, Nigerian Metallurgical Society Publishers, National Technical Secretary, Nigerian Metallurgical Society. He has also served as an external assessor to many international bodies among which are the National Center of Science and Technology Evaluation Ministry of Education and Science Astana, Republic of Kazakhstan. Anna University Centre for Research Chennai, India. University of Johannesburg, Nova Science Publishers Inc Hauppauge USA. National Research Foundation (NRF), South Africa, just to mention a few. He has Published 235 papers in peer-reviewed International and National Journals, papers in peer-reviewed International and National conference proceedings, papers in peer-reviewed micrographs and chapter in peer-reviewed book. Prof Aigbodion is a National Research Foundation (NRF) South Africa C3 rated researcher.

Prof Nita Inderlal Sukdeo is currently an Associate Professor and Head of Department in the Department of Quality and Operations Management within the School of Mechanical and Industrial Engineering at the University of Johannesburg, South Africa. She obtained a Masters in Quality from the Durban University of Technology and a PhD in Engineering Management from the University of Johannesburg. She is an active researcher in the field of total quality management and operations management. Her field of expertise also include advanced manufacturing technologies, smart factory, Quality 4.0, quantitative analysis, quality management systems, quality auditing and risk assessment. She is a qualified Lead Auditor, proficient in ISO standards and certification. She is chairperson and director of the Society for Operations Management in Africa (SOMA), a non-executive director of the South African Society for Quality (SASQ). She is an active participant and session chair of the IEOM Women in Industry and Academia panel session Africa edition.