Explicit microstructure and electrical conductivity of epoxy/carbon nanotube and green silver nanoparticle enhanced hybrid dielectric composites

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\textbf{ABSTRACT}

Carbon nanotubes (CNTs) decorated with silver nanoparticles (AgNPs) are promising nanomaterials for improving the dielectric properties of polymer materials for energy storage and micro-capacitor applications. However, the cost of AgNPs limits their wide application. This work describes the synthesis of green silver nanoparticles (GAgNPs) from cashew leaves and their hybridization with CNTs. These new hybrid nanocomposites were developed by adding 0.1, 0.2, 0.3, 0.4 and 0.5\% CNTs and 0.5\% GAgNPs in an epoxy matrix. Electrical conductivity, dielectric constant, and capacitor raised as CNTs content increased from 0.1 to 0.5\% with 0.5\% GAgNPs. The high dielectric constant reported in this work was made possible because of the high electron mobility of GAgNPs, which helps to enhance the conductivity of the epoxy. The highest electrical conductivity and dielectric constant were obtained for hybrid nanocomposites based on 0.5\% CNTs and 0.5\% GAgNPs. It was established that GAgNPs modified CNTs can be used to enhanced the electrical conductivity, dielectric constant and capacitance of epoxy resins for isotropic conductive adhesives, assemblies, and electronic packaging applications.

1. Introduction

In recent years the development of conducting polymer composites through the addition of electrically conductive nanomaterials for electronic devices, sensors, adhesives, and electromagnetic interfaces has been well studied [1,2]. Electrical conductive fillers such as metal powders, graphite, and carbon black have been used to achieve a percolation threshold condition at around 10–50\%. This high percentage of filler addition usually lowered the mechanical properties of the composites as a result of agglomeration of the particles in the polymer matrix [3,4]. In order to avoid this limitation and create conductive polymer composites with good mechanical properties the use of conductive nanoparticles such as carbon nanotubes (CNTs), graphite, and carbon black (CB) nanoparticles have been used to improve electrical conductivity and mechanical properties for electronic device applications [5]. CNTs are particularly attracting the attention of researchers due to their high electrical conductivity and low percolation threshold. However, despite their high electrical conductivity, their entangled nature makes them difficult to disperse in polymeric matrices, while their high cost limits their use in practical electronic devices [6].

Ma et al. [7] reported on the electrical conductivity of epoxy hybrid composites based on CNTs and CB. The mechanical and electrical conductivity were determined. They observed that the addition of CNTs to CB greatly enhanced electrical conductivity. They also observed a low percolation threshold of 0.2\% CB and 0.2\% CNTs while achieving a good ductility and fracture toughness.
Ma et al. [8] also reported the enhancement of the electrical conductivity of epoxy/carbon nano-tube-coated-silver nanoparticles (CNT + AgNP). The microstructure, mechanical, thermal, and electrical properties of the developed hybrid composites were determined. The mechanical properties of epoxy/CNT and epoxy/CNT + AgNP systems were similar while electrical conductivity was enhanced for the epoxy/CNT + AgNP nanocomposites.

Dorigato et al. [9] reported the improvement of electrical conductivity of epoxy/carbon fiber (CF) composites. They observed that there was a decrease in glass transition temperature (Tg) after the addition of CF and CB with a higher electrical conductivity being achieved than for pure carbon fiber based systems. Krainoi et al. [10] reported on AgNP decorated CNTs for natural rubber (NR) composites. They observed a stronger network formation after incorporation of AgNP into the NR matrix due to an interaction between the CNT and AgNP. Dhibar and Das [11] reported on the properties of polyaniline (PANI)/CNT composites decorated with AgNPs for supercapacitors. Their nanocomposite had better electrical conductivity at room temperature and showed nonlinear current – voltage characteristics. Yusof et al. [12] studied the electrical, thermal and microstructural properties of multi-walled CNTs with AgNPs. As mentioned earlier, despite the high demand for CNTs, there remains the issue of poor dispersion, entanglements and high cost of CNTs limiting their use in electronic devices [13–15]. Also from the above literature, it was observed that the used of AgNPs to enhance the electrical conductivity of polymer/CNT composites is promising. However, the cost of silver is even higher than that of CNTs and further restricts the application of polymer/CNT + AgNP composites. The high cost of silver used in improving the electrical conductivity of epoxy/CNT composites motivated interest in the development of epoxy/CNT + AgNP nanocomposites based on green AgNPs synthesized from plant extracts. Researchers [16–19] have, for example, reported that cashew leaves are acidic in nature and contains anacardic acids which are antibacterial agents that can be used in the reduction of Ag⁺ to Ag. Cashew products have been previously exploited in nanotechnology [19] and the use of green plant extracts to synthesize AgNPs may not only reduce cost but may also be more ecofriendly.

2. Materials and method

The CNTs were purchased from Hongwu International Group (China). The CNTs are multi-walled CNTs with average diameters of 10–40 nm and 10–20 μm lengths (see Figure 1).

The GAgNPs were synthesized using cashew leaves. The fresh cashew leaves used in this work were obtained from the surroundings of the University of Nigeria (Nsukka, Nigeria). The fresh leaves were washed with distilled water and dried. 100 ml of ethanol was then added to the washed cashew leaves and left for 1 hr, after which a solution of AgNO₃ (100 ml) was added. The addition of AgNO₃ to the cashew leaf extract samples produced an instant color change from an original, yellow solution to a dark brown solution (see Figure 2a). The reaction was left for 30 min before heating in an electric oven at 100°C under stirring with a speed of 2000 rpm, after heating the solution was centrifuge for 1 hr to obtain the solid GAgNPs.

The functionalization of the CNTs was done using 65% HNO₃ and 30% H₂O₂. The CNTs were first treated with 100 ml for 5 hrs, then deionized water was added to the solution and was filtrated. The filtered product was diluted to obtain a Ph of neutral. The H₂O₂ was added to obtain carboxylic acid functionalized CNTs [20]. Before the preparation of the epoxy based nanoparticles the CNT + GAgNP was dissolved in ethanol and was degassed to reduce air in the formulation and remaining ethanol at 75°C for 4 hrs. The treated CNT + GAgNPs were then added to epoxy (Araldite LY556, Ciba Geigy) by varying the CNT loading from 0.1, 0.2, 0.3, 0.4 to 0.5 wt% using a constant GAgNP loading of 0.5 wt%. The hardener (HY951, Ciba Geigy) was then added and the mixture was cast into a wooden

Figure 1. TEM image of CNTs.
mold and cured at 75°C for 4 hrs. The samples were then post-cured at 120°C for 2 hrs. The morphology and particle size of the CNTs, AgNPs, and hybrid CNT + GAg.NPs were determined by transmission electron microscopy (TEM) using a model Jeol JEM-2100F. The produced composites are displayed in Figure 3.

The electrical conductivity, capacitor and dielectric constant measurements were conducted using the Kaise insulation test (model SK5010). The test was determined by placing the samples between two electrodes. The capacitor and dielectric constant were determined by varying the frequency from $10^3$ to $10^6$ Hz. The electrical conductivity was calculated using Equation 1.

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

The dielectric constant was calculated using Equation 2.

$$\varepsilon^1 = \frac{C_p(A)}{A(\varepsilon_0)}$$  \hspace{1cm} (2)

where: $A$ is the area, $d$ the thickness, $C_p$ is the capacitance, $\varepsilon_0$ is the dielectric constant of free space, and $\rho$ is the electrical resistivity.
A VEGA 3 TESCAN model scanning electron microscope (SEM) was used to determine the various microstructures obtained. An X’Pert Pro diffractometer (XRD) was used for the identification of the different phases.

3. Results and discussion

3.1. TEM analysis

TEM analysis was used to determine the size and shape of the AgNPs. The result of the TEM imaging of the synthesized green AgNPs is shown in Figure 4a. From Figure 4a it was can be seen that round and spherical shapes are visible. The composite microstructure shows well distributed nanoparticles without major clustering of particles. A particle size range from 45–65 nm was observed. The EDS shows higher peaks of the Ag element. This confirms the high Ag signal and the formation of AgNPs. The purity of the green AgNPs produced was high as there is not any oxygen or silver compound formed as displayed by the EDS. This was attributed to the fact that a reduction was obtained. A similar observation was reported in [21].

Figure 5 shows the EDS image of the CNT + GAgNPs. It was observed that there was a significant change in the CNT structure after the addition of the GAgNPs. The GAgNPs alter the multi-walled structure of the CNTs. The EDS revealed high peaks of C and Ag which is on par with the work reported in [21,22].

The bonding between the CNTs and the GAgNPs was good after the decoration of GAgNPs on the surface of the CNTs. Well adhering GAgNPs onto CNTs were observed in this work. This shows that GAgNPs and CNT’s surfaces were in good contact as can be seen clearly in the TEM image in Figure 5a. The good bonding and adherence of the GAgNPs to the CNTs surface was attributed to the functionalization of the CNTs [22,23].

3.2. XRD analysis

The XRD spectrum obtained is displayed in Figure 6 where it was observed that the AgNPs were well attached to the CNTs. Proper bonding obtained is attributed to the functionalization of the CNTs. There was a significant change in the XRD patterns of all the samples in question. The XRD pattern of the epoxy
polymer shows an amorphous phase which is a clear feature of epoxy materials. Crystalline phases were observed in the GAgNPs and CNTs. The graphite crystalline phases in the CNTs as revealed by the XRD analysis are: (100), (102) and (110), respectively. This is on par with the XRD analysis observed in [1,24]. The XRD patterns of GAgNPs revealed silver metallic phases of (111), (200), (220) and (311), respectively.

Figure 5. TEM/EDS image of CNTs + GAgNPs.

Figure 6. XRD spectrum of the various samples.
The addition of 0.5% GAgNPs and 0.5% CNTs to the epoxy resin altered the amorphous nature of the neat polymer to a two phase amorphous-crystalline system. The presence of the hybrid nanofilars was the main reason for the crystalline (111) and (200) phases (GAgNP) and (100) phases (CNT) as observed in the XRD spectrum (see Figure 6). The binding energy between GAgNPs and CNTs observed in this work was attributed to the funtion-alization of the CNTs, which improved the bonding and reactivity with GAgNPs [25]. The GAgNPs produced more diffraction peaks in all the samples under investigation. Equation 3 was used to determine the crystallite size of the GAgNPs, CNTs, and epoxy/CNT + GAgNP composites. It was observed that a crystallite size of 7.56 nm, 10.45 nm, and 15.56 nm was observed for the GAgNP, CNT, and epoxy/CNT + GAgNP systems, respectively.

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

(3)

### 3.3. SEM analysis of the composite samples

The SEM images of the composites are displayed in Figure 7. It is clear from these images that there was quite a difference in the morphology between the different samples. Figure 7a shows the microstructure of the neat epoxy polymer. However, the addition of 0.2%CNT + 0.5% GAgNP and 0.5% CNT + 0.5% GAgNP altered the epoxy microstructure significantly (see Figure 7b and 7c). As the amount of GAgNP and CNT increased in the epoxy, the amount of nanoparticles become more clearly visible in the SEM. The presence of GAgNP and CNT can be seen clearly as white dots in the epoxy matrix. These white phases may raise free electrons and improve conductivity, energy storage ability and strength of the polymer composite.

### 3.4. Electrical conductivity

The addition of CNTs and GAgNPs increased the electrical conductivity of the epoxy. It was observed that an electrical conductivity of \(5.6 \times 10^{-13}\) S/cm was obtained for the pure epoxy, which is within the range reported for epoxy [16]. The addition of CNTs and GAgNP decorated CNTs greatly improved the electrical conductivity. It can be observed in this work that both epoxy/CNT and epoxy/CNT + GAgNP composites resulted in an increase electrical conductivity (see Figure 8), however the epoxy/CNT + GAgNP hybrid system showed a higher increment in electrical conductivity than the epoxy/CNT composites. The higher electrical conductivity for the epoxy/CNT + GAgNP was attributed to the higher electrical conductivity of AgNPs [21]. The electrical conductivity of the epoxy polymer has been enhanced from \(5.6 \times 10^{-13}\) S/cm to \(4.8 \times 10^{-3}\) S/cm for epoxy/0.5%CNT and \(9.1 \times 10^{-3}\) S/cm for epoxy/0.5%CNT + 0.5%GAgNP. The higher electrical conductivity observed can be also attributed to the higher surface area to volume of the GAgNPs which helps to create conductive pathways in the polymer resin [12].

### 3.5. Dielectric constant

The dielectric constant is an important property in the electrical industry and is the ratio of electric permeability of the sample to the electric permeability in vacuum. It was observed that the dielectric constant of the composites decreased as the frequency increased. This decrease in dielectric constant as a function of frequency can be attributed to the polarization of polar groups in the samples, which may not be as easy as frequency rises [26]. The dielectric constant of the composites is higher than that of the neat epoxy resin. For example, a dielectric constant of 1200, 980, 650 and 400 was recorded at 10^3 Hz, 10^4 Hz, 10^5 Hz and 10^6 Hz for epoxy/0.5%CNT + 0.5%GAgNP hybrid composites (see Figure 9). The raise in dielectric constant of composites with CNTs and GAgNPs was attributed to the higher electrical conductivity of CNTs decorated with GAgNPs. However, epoxy/0.5%CNT + 0.5%GAgNP hybrids had the highest dielectric constant of all the samples under investigation. The epoxy/0.5%CNT + 0.5%GAgNP composite can sustain electric charges for a longer period of time than the other samples. The ability of the epoxy/0.5%CNT + 0.5%GAgNP to withstand higher electric charges could be attributed to the movement of the CNTs and GAgNPs, which form conductive pathways in the epoxy matrix and hence raise the electrical conductivity with an increase in surface charge reorientation. The high dielectric constant reported in this work was made possible because of the high electron mobility of GAgNPs and helps to enhance the overall conductivity of the epoxy system. It was demonstrated that the highest electrical conductivity and dielectric constant was obtained for the epoxy/0.5%CNT + 0.5%GAgNP nanocomposites, which makes them of interest for the production of e.g. smart actuators.

### 3.6. Capacitance

In this work, it was observed that the capacitance of the materials increased with the addition of CNTs and GAgNPs and reduced as the frequency increased (Figure 10). The decreased in capacitance with frequency could be attributed to the fact that an equilibrium within the electric field was not able to form as a result of dipole relaxation [26]. The capacitance of the developed material rose from \(2.3 \times 10^{-11}\) F to \(2.8 \times 10^{-7}\) F at 10^9 Hz for epoxy/
0.5% CNT + 0.5% GAgNP. The high capacitance observed results from the formation of micro-capacitance around the polymer network, which increases with as the number of CNTs and GAgNPs in the formulation and the polarization of charges at the materials interfaces. The uniform distribution of CNTs and GAgNPs enhanced the energy storage ability of the developed materials.

4. Conclusions

New hybrid nanocomposites were developed based on epoxy, CNTs, and green AgNPs to be used for energy storage in microelectronic devices. The electrical conductivity, dielectric constant, and capacitance rose with CNT content from 0.1 to 0.5% and 0.5% GAgNPs. The high dielectric constant reported
in this work was originated from the high electron mobility of GAgNPs, which helped to enhance the electrical conductivity of the epoxy composites. It was also shown that the highest electrical conductivity and dielectric constant were obtained for epoxy/0.5%CNT + 0.5%GAgNPs hybrid nanocomposite. It was established that GAgNP decorated CNTs can be used to further improve the electrical conductivity, dielectric constant and capacitance of epoxy/CNT composites for applications in conductive adhesives, assemblies and electronic packaging.

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Disclosure statement

There is no conflicts of interests to report in this work.

Notes on contributor

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