CONDUCTIVITY ENHANCEMENT FOR CARBON NANOTUNES WITH SILVER DECORATION

W. Thitsartarn1,*, C. C. Yeo Jayven1, C. B. He1,2,*
1 Institute of Materials Research and Engineering, 3 Research Link, Singapore
2 Department of Materials Science & Engineering, National University of Singapore, Singapore
* Corresponding author (cb-he@imre.a-star.edu.sg and thitsartarnw@imre.a-star.edu.sg)

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1 Introduction

Epoxy resin-based CNT composites have been extensively investigated in view of their potential applications in the electronics, aerospace and automotive industries [1]. One of the approaches to the development of conductive thermoplastics is to add conductive fillers into a non-conductive polymer matrix. There are many commonly-used conductive fillers such as metal powders, metal fibers, carbonaceous materials, etc [2–8].

Carbon nanotube is one of the most interesting conductive fillers due to the morphological and chemical advantages (i.e., high surface-to-volume ratio, good thermal and electrical conductivity, lightweight and etc) [9-14]. The electrical conductivity of the composite was remarkably improved by adding some amount of CNTs into epoxy [15,16]. The increase in CNT content can enhance the electrical conductivity of composites; however, the solution viscosity becomes too high to produce void-free composites when the CNT volume is too large. This leads to the contradictions between material processing and high electrical conductivity.

Integration of CNT and metal fillers is one of the potential solutions to enhance the electrical conductivity of the nanocomposite by incorporation of metal nanoparticles on surface of CNT using simple deposition-precipitation at room temperature. The product has been used as a conductive filler in epoxy nanocomposite and composite laminate CFRP. The electrical conductivity, thermal and mechanical property of nanocomposite and the composite CFRP have been investigated.

2 Experimental

2.1 Materials

Research grade thin-multi-walled carbon nanotubes (TMWCNTs) were purchased from Nanocyl®. AgNO₃ and 3-aminopropylmethoxysilane (APTMS) were purchased from Aldrich. NaOH was purchased from Merck. Araldite® LY 1564 epoxy resin and Aradure® 3487 hardener from Huntsman were used in this work.

2.2 Silver nanocrystal decoration of thin-multi-walled carbon nanotubes (TMWCNTs)

Amine-functionalized TMWCNTs were dispersed ultrasonically in DI water before mixed with AgNO₃ solution, followed by adding NaOH for pH adjustment. The suspension was stirred vigorously before separated by centrifugation. After washed with DI water to remove the excess sodium nitrate, the final product was kept in DI water. The sample is designated as Ag-TMWCNT.
2.3 Fabrication of conductive nanocomposite

The Ag decorated TMWCNT (Ag/TMWCNT) was washed and dispersed in ethanol using ultrasonicator before added into the epoxy resin. The mixture was homogenized, followed by solvent removal. After cooling down to room temperature, the hardener was added (Resin: Hardener = 100g: 34g). The resin dough was put into glass-mould, and cured at 100 °C for 5 h in air. The final product was measured the electrical conductivity using a four-probe resistivity meter following ASTM D257 standard, the tensile and flexural property, following ASTM D 638-03, D 790-03 tensile. The storage modulus of the nanocomposites were measured by Dynamic-Mechanical Analyzer (DMA, Thermal Instruments), working temperature range is –room temp to 150°C. In addition, the charge density on the surface of nanocomposite was investigated using Finite Element Method for simulation.

2.4 Fabrication of composite laminate

![Vacuum bagging setup for conductive CFRP composite laminate](image)

Fig 1. Vacuum bagging setup for conductive CFRP composite laminate

The developed conductive composite laminate was fabricated using hot-press curing under vacuum. Namely, the Ag-TMWCNT/epoxy nanocomposite was laminated onto the woven carbon fiber fabric using wet lay-up process. The total fiber layer of 16 plies with fiber orientation of 0°. The fiber content in CFRP was 70 ± 3 wt%. The uncured laminated CFRP was put into the vacuum bagging which connected to the quick-disconnect set, as shown in Fig. 1. The set up was pressed between two plates of the hot press machine (Labtech LP25M, Labquip Pte Ltd). The vacuum was applied to the fabricated material while the pressure was slowly increased from 0 to 61 bars at 25 °C. After the pressure was constant at 61 kPa, the curing temperature was increased to 100 °C and maintained for 5 h. The similar fabrication process was applied to the neat epoxy and TMWCNT/epoxy CFRPs.

3 Results and Discussion

3.1 Silver decorated thin-multiwalled carbon nanotubes

The Ag nanoparticles were decorated on the functionalized TMWCNTs using simple deposition-precipitation of AgNO₃ and NaOH at room temperature.

![Scheme 1. Proposed reaction mechanisms for the deposition of silver nanocrystals at amine groups of functionalized TMWCNTs](image)

Scheme 1 shows the proposed reaction mechanism for deposition of Ag particles on the surface of functionalized TMWCNTs. The amine groups on the surface of functionalized
TMWCNTs interact with AgNO₃ to form –NH⁻ Ag⁺ complexes, and then reduced by hydroxyl groups (–OH), generated by NaOH, resulting in the Ag particles depositing on the surface of the TMWCNTs.

Fig 2. FESEM images of Ag-decorated functionalized TMWCNTs

Fig 2a and Fig 2b shows the functionalized TMWCNT decorated by Ag nanoparticles at the different positions of TEM samples. Both figures show that the good dispersion of Ag particles on the surface of functionalized TMWCNTs with the relatively small and homogeneous particle size (i.e., the average size is < 5 nm). However, some big clusters of aggregated Ag and some empty surface of TMWCNTs were observed, as shown in Fig 2c.

The XRD diffraction pattern of the functionalized TMWCNTs and Ag/TMWCNTs (pH 7.5, 0.05 M AgNO₃, aging time 60 min) is presented in Fig 3. The small peak at ~ 25° corresponds to the amorphous carbon of the carbon nanotubes and the peaks at 38.1°, 44.3°, 66.4°, 78.4°, and 81.6° were indexed to the (111), (200), (220), (311), and (222) planes of the Ag crystal structure, respectively [17,18]. Silver oxide compounds (i.e., Ag₂O and AgO) were also observed, as evidenced by the diffraction peaks at ~33.1°, 54.9°, 68.7° for Ag₂O, and the peak at 64.5° for AgO [19]. This result suggests the mixed phases of Ag contained in the synthesized CNT-based filler.

3.2 Electrical and mechanical properties of silver-decorated carbon nanotubes filled epoxy resin (Ag-TMWCNT/Epoxy)
The synthesized Ag-decorated TMWCNT was used as a conductive filler to enhance the electrical conductivity of epoxy resin. Table 1 shows the electrical conductivity of neat epoxy resin and the developed nanocomposites with Ag nanoparticles and Ag-decorated TMWCNTs with various filler contents. With 1 wt% of Ag nanoparticles, the electrical conductivity of the composite increased ca. 100 times due to the presence of conductive fillers in the polymer matrix. Meanwhile, the electrical conductivity of the composite increased ca. 10^6 times with 0.2 wt% of functionalized TMWCNTs. The remarkable increase of the electrical conductivity of nanocomposite with low content of TMWCNT filler is due to the high surface-to-volume ratio or the bulkiness of conductive CNT fillers [15,20-23].

With 0.2 wt% of Ag-TMWCNT filler, the electrical conductivity of the Ag-TMWCNT/Epoxy nanocomposite increased ca. 10^8, as compared to the electrical conductivity of neat epoxy resin. Interestingly, as compared to the same filler content, the electrical conductivity of nanocomposite containing Ag/TMWCNTs was ca. 10-100 times higher than that of nanocomposite containing only functionalized TMWCNTs. The higher electrical conductivity of Ag-TMWCNT/Epoxy nanocomposite is due to the attachment of Ag particles onto the defect sites of TMWCNT surface that compensates the above negative effect by enhancing the conductivity of CNTs and reducing the contact resistance of CNT junctions in matrix [9].

![Cross section of Ag-decorated functionalized TMWCNTs filled epoxy resin nanocomposite with (a) 1 wt% and (b) 0.8 wt% fillers content](image-url)

The result in Table 1 clearly shows that the electrical conductivity of TMWCNT/Epoxy and Ag-TMWCNT/Epoxy nanocomposite increased with filler content. However, the physical appearance and texture of the nanocomposite was not homogeneous when the filler content was high. Namely, there are many visually observable voids in the matrix of the Ag-TMWCNT/Epoxy nanocomposite (as shown in Fig 4a) when the filler content reached 1 wt%. The same phenomenon was also observed on the TMWCNT/Epoxy nanocomposite. The formation of voids in the nanocomposite matrix is due to the high viscosity of the resin dough, leading to the difficulty of air or vaporizable chemicals to release from the polymer matrix. In order to obtain the void-free nanocomposite, the 0.8 wt% filler content, which is the maximum filler content, is recommended for further study (Fig 4b).
Fig 5. Flexural, tensile and storage modulus of neat epoxy, Ag-decorated functionalized TMWCNTs filled epoxy resin (Ag-TMWCNT/Epoxy, 0.8 wt% filler) and functionalized TMWCNTs filled epoxy resin (TMWCNTs/Epoxy, 0.8 wt% filler) composite

The mechanical property of the developed nanocomposite with the filler content of 0.8 wt% was evaluated via its flexural, thermal and storage modulus and the result was shown in Fig 5. The tensile and flexural modulus of Ag-TMWCNT/Epoxy and TMWCNT/Epoxy composite was slightly lower, but the storage modulus was higher, as compared to neat epoxy resin. The decrease of the tensile and flexural modulus of the nanocomposite with fillers is (1) due to the presence of the filler with large volume [9,20] and (2) due possible to the imbalance of the crosslinking functional groups [24-26]. In overall, the mechanical property of epoxy resin was retained after addition of the filler, suggesting that the reinforcement effect due to Ag/TMWCNTs in composites was not sacrificed after Ag decoration.

Thermal property of the nanocomposite was evaluated via glass transition temperature (T_g), using Dynamic-Mechanical Analyzer or DMA. Neat epoxy resin shows the estimated T_g around 85 °C, and the result is in good accordance with the T_g reported in the materials data sheet from the company (i.e., 81-87 °C). Meanwhile, the T_g of TMWCNT/Epoxy and Ag-TMWCNT/Epoxy were around 75 °C and 76 °C, respectively. The decrease of the T_g of nanocomposite after filler addition is due to the fact that fillers in composites increase the free volume and loosen the molecular packing of the polymers, which results in a decrease of the T_g with increasing filler loading [17,27].

3.3 Electrical and mechanical properties of conductive CFRP laminated with silver-decorated carbon nanotubes filled epoxy resin (CFRP Ag-TMWCNT/Epoxy)

The developed nanocomposite with 0.8 wt% filler content was used to laminate on the woven carbon fiber fabric and cured using hot-press and vacuum bagging, as shown in Fig 1.

Fig 6. Electrical conductivity of CFRP laminated with neat epoxy, Ag-decorated functionalized TMWCNTs filled epoxy resin (Ag-TMWCNT/Epoxy, 0.8 wt% filler) and functionalized TMWCNTs filled epoxy resin (TMWCNTs/Epoxy, 0.8 wt% filler)

The electrical conductivity of the CFRP with neat epoxy resin, TMWCNT/Epoxy and Ag-
TMWCNT/Epoxy nanocomposite is presented in Fig 6. The CFRP containing neat epoxy showed some positive electrically conductive value, suggesting that the CFRP can conduct some electricity. As shown in Section 3.2, the electrical conductivity of neat epoxy resin was very low (~6.5 x 10^{-15} S/cm); therefore, the electrical conductivity of the CFRP with neat resin is principally due to the conductive property of carbon fiber.

Substitution for developed nanocomposite resin can improve the electrical conductivity of the CFRP laminated. The electrical conductivity of CFRP with TMWCNT/epoxy nanocomposite increased about 100 times, as compared to the CFRP laminated with neat epoxy resin. Interestingly, the conductivity of CFRP containing Ag-TMWCNT/epoxy nanocomposite rose up to 1000 times higher than the counterpart containing neat epoxy resin and increased 10 times higher than the CFRP with TMWCNT/Epoxy nanocomposite. The increase of the electrical conductivity of the CFRP with the developed nanocomposite resin is due to the increased of the conductive property of the matrix, which could enhance and/or increase the pathway of electrons transfer. As a result, the significant improvement of electrical conductivity of CFRP was observed. The result in this section suggests that combination of carbon nanotubes and metal fillers can synergistically enhance the electrical property of the conductive composite laminate and it can clearly prove our assumption about hybrid-filler system to improve electrical property of the conductive composite laminate.

Fig 7 shows the mechanical properties (evaluated by tensile, flexural and storage modulus) of carbon-reinforced laminate using developed conductive resin, compared to the CFRP with neat epoxy resin. The flexural, tensile and storage modulus of CFRP with TMWCNT/Epoxy nanocomposite was lower than that of CFRP with neat epoxy. It is possible due to the large volume of carbon nanotube fillers dispersing in the epoxy matrix [9,20].

Interestingly, the CFRPs with Ag-TMWCNT nanocomposite showed the better mechanical properties than that with only TMWCNTs for flexural modulus and even better than that with neat epoxy resin for tensile and storage modulus. The reason for this improvement is still unclear; however, it is possible due to the small amount of solid metal filler on the matrix which assist to improve the mechanical property of the CFRP [28-29].

Fig 7. Flexural, tensile and storage modulus of CFRP laminated using neat epoxy, Ag-decorated functionalized TMWCNTs filled epoxy resin (Ag-TMWCNT/Epoxy, 0.8 wt% filler) and functionalized TMWCNTs filled epoxy resin (TMWCNTs/Epoxy, 0.8 wt% filler)
penetrate through the layer. It suggests that the transportation of resin into the fiber fabrics was not hindered by the addition of Ag-TMWCNT/Epoxy nanocomposite resin.

Fig 8. (a) Fracture surface of CFRP laminated using Ag.decorated functionalized TMWCNTs filled epoxy resin (0.8 wt% filler) and (b) its closed-up image.

The interlaminar fracture toughness (represented as the strain energy release rate, $G_{ik}$) of the CFRP with neat epoxy was ca. 660 ± 5 J/m² whereas the $G_{ik}$ of the CFRP with Ag-TMWCNT/Epoxy nanocomposite was 740 ± 4 J/m². The higher $G_{ik}$ of CFRP with Ag-TMWCNT/Epoxy nanocomposite is due to the strong filler–epoxy bonding, which was formed through the linkage between amine groups of APTMS functionalized on the surface of TMWCNTs [30].

In order to use this composite material for extreme applications, the capability of the material to carry or conduct the intensive charge on the surface or in the matrix should be studied. This material property is important for some extreme application such as lightning strike protection, conductive container/infrastructure. Therefore, in this work charge dispersion was evaluated using the lightning strike simulation based on Finite Element Method (data is not presented here). It was found that the charge generated by the lightning strike simulation accumulated on the surface of CFRP with neat epoxy resin. Meanwhile, the dispersion of the charge on the surface of CFRP with the developed nanocomposite resin was relatively good, less charge accumulation. The simulation result suggests its good charge carrying property of the newly-developed conductive CFRP. For the charge penetration into the matrix, the electric field drops significantly ~ 0.5 mm below the top surface of the specimen at its center around the charge generating point. This result suggests that the developed nanocomposite laminate can shield a large amount of electric field.

4 Conclusion

Ag.decorated TMWCNTs were successfully synthesized via a simple deposition-precipitation of AgNO₃ and NaOH at room temperature. The electrical conductivity of epoxy resin significantly increased after adding this product to the resin matrix. Furthermore, the mechanical property of epoxy resin was not sacrificed by adding this filler. The results of this study indicate that the Ag/TMWCNT is the potential conductive filler with mechanical
enhancement property for many applications such as conductive container/infrastructures.

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References