Synergistic electrical and thermal transport properties of hybrid polymeric nanocomposites based on carbon nanotubes and graphite nanoplatelets

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A B S T R A C T

In this study hybrid ternary polymeric nanocomposites based on carbon nanotubes (CNTs) and graphite nanoplatelets (GNPs) are examined for their enhanced transport properties, over mono-nanofiller composite systems, originated via a synergy mechanism. Using an epoxy as the host matrix, a number of CNTs/epoxy, GNP/epoxy and hybrid CNTs/GNP/epoxy specimens are processed and their electrical and thermal properties are characterized. Furthermore, these transport properties are also estimated using a set of recently developed computational models based on percolation analysis and statistical continuum mechanics. Results suggest that the models, in agreement with the experimental observations, confirm the presence of the synergy effect for both the electrical and thermal transport properties. Both the computational and experimental studies suggest incorporating miniscule amount of auxiliary nanofiller (ex. 10%wt CNTs compared to GNP), boosts the electrical conductivity of the hybrid composites by several orders of magnitudes. Furthermore, the experimental measurements and the strong contrast computational models suggest that, owing to the formation of the hybrid CNT/GNP network, the hybrid CNT/GNP/polymer nanocomposites outperform their single-nanofiller counterpart configurations. The investigation affirms that the particle agglomeration severely affects the transport properties of the hybrid nanocomposites and it is the root cause for the conflicting results in the literature.

1. Introduction

Polymeric nanocomposites comprise a polymeric host matrix and at least one nanostructured filler phase with enhanced physical properties. Among the most utilized nanofillers are carbon nanotubes (CNTs) and graphite nanoplatelets (GNPs) due to their exceptional mechanical, electrical and thermal properties. Nanocomposites based on CNTs are widely employed as electro conductive materials [1,2]. The advancement of integrated circuits (ICs) and high power density communication devices is tied to the evolution of high performance thermal interface materials (TIMs). Common TIMs are composite materials comprising a host matrix and a highly conductive filler phase. In this regard, GNP are very promising nanofillers for TIMs [3]. To further enhance the transport performance of carbon nanofillers based composites, ternary hybrid CNT/GNP/polymer nanocomposites were pondered. For example, single wall and multiwall CNTs combined with GNP in variety of forms like graphene nanosheets (GNS), exfoliated graphite (EG) and reduced graphite oxide (rGO) have shown extraordinarily enhanced thermal conductivities [4–7]. Hybrid porous
electrodes made from CNTs and reduced graphite oxide (rGO) were deemed very feasible for the new generation of high energy density super capacitors [8,9]. Furthermore, hybrid CNT/GNP nanocomposites have been employed in dye-sensitized solar cells (DSSCs) to boost the power generation performance by enhancing the dye adsorption and charge recombination processes [10]. Other hybrid nanocomposites have been utilized as thin films in the solar cells to tailor their electrical conductivity and optical transparency [11]. Beyond the enhancement of the transport properties, hybrid CNT/GNP/polymer composites exhibit enhanced storage and loss moduli [12], static mechanical properties [13] and dielectric properties [14].

Despite the several envisioned applications for the hybrid CNT/GNP polymer nanocomposites, the early attempts to optimize their electrical conductivities were not successful [7]. Actually, several studies reported inconsistent levels of the electrical conductivity improvement upon hybridization [6,15–19].

In an attempt to probe these inconclusive and conflicting experimental results, the electrical and thermal properties of binary polymeric nanocomposites were investigated computationally [20].

Geometrical concepts like the excluded volume and the interparticle distance (IPD) provided the basis for several models in investigating the effects of the filler’s shape, size, aspect ratio [2,21–23] and its state of dispersion and agglomeration [24,25] on the electrical percolation threshold. In the vicinity of the percolation threshold, the electrical conductivities of these single-nanofiller systems have been predicted by the classical percolation law [26]. More rigorous models have been developed to explain the electrical conductivity of these nanocomposites below the percolation threshold; the so-called dielectric region, to right above it [27,28]. According to these studies the electrical conductivity in randomly distributed particulate-based nanocomposites are mainly governed by the electrical tunneling mechanism, first introduced by van Beek [29] and Frenkel [30].

Similarly, the thermal conductivity of binary polymeric nanocomposites based on CNTs or GNP s have been investigated computationally. In an early study, the effective medium approach was utilized to compare the viability of GNP s and CNTs to enhance the effective thermal conductivity of a polymeric host [31]. Other approaches were utilized to investigate the thermal conductivity of ordered heterogeneous nanocomposites based on the classical homogenization techniques [32].

Most of the computational investigations of the electrical and thermal properties of polymer nanocomposites are strictly limited to binary nanocomposites systems with ideal microstructures. These ideal assumptions restrain the feasibility of these models since particulate nanocomposites are prone to uneven distribution and poor dispersion of the nanofillers. The conflicting reported results of several experimental studies of the electrical and thermal properties of the hybrid CNT/GNP/polymer systems could be contingent to these difficulties.

Alternatively, for randomly disordered composite systems, the transport properties can be evaluated computationally using statistical continuum approaches [33,34]. On this basis, to investigate the effective electrical and thermal conductivities of a hybrid ternary nanocomposite, two computational models were recently developed by the authors [35–37]. These models assume a general and more realistic random distribution of the nanofillers within the polymeric matrix, which extends their applicability to the composites with nanofiller’s shape imperfections, deformations and agglomerations.

In the current study, these models are employed to estimate the electrical and thermal conductivities of hybrid CNT/GNP/epoxy nanocomposites by taking into account the particle aggregation and deformation defects. To scrutinize the validity of the models and to probe the basis of the synergy effect between the two nanofillers, a number of CNT/GNP/epoxy nanocomposite configurations are also processed and their morphologies together with their thermal and electrical properties are characterized. The state of deformation and agglomeration of the embedded CNTs and GNP s is quantified and utilized later in the computational study. Finally, the model predictions of the electrical and thermal conductivities are compared to the experimental measurements to explore the prospects of the synergy mechanism and its driving forces.

2. Experimental study

2.1. Samples preparation

A number of CNT/polymer, GNP/polymer and hybrid CNT/GNP/polymer nanocomposites specimens were processed. For the CNT/polymer and the GNP/polymer specimens, five different configurations were prepared comprising 1.0–5.0%wt of the CNTs and the GNP s, respectively. For the hybrid CNT/GNP/polymer specimens five different configurations were selected as well; each comprising (X)%wt GNP and (X/10)%wt CNT were X = 1.0–5.0.

Exfoliated graphite nanoplatelets (x-GNPs) were supplied by XG-Sciences, Inc., with average particle diameter of 5.0 microns and thickness of 6.0–8.0 nm (i.e., nominal aspect ratio = 650–850). Short length multiwall carbon nanotubes (MWCNTs) were supplied by Cheap Tubes, Inc., with outer diameters of approximately 8.0 nm and lengths in the range 0.5–2.0 µm (chemical purity >95.0%). The hosting polymeric matrix is a bisphenol-A epoxy vinyl ester resin (Derakane 411–350) supplied by Ashland, Inc., along with suitable hardener (Norox MEKP-925H) and promoter (Cobalt Naphtenate-6.0%) according to the supplier’s recommendation. The high purity non-ionic surfactant Triton X-100 was supplied by Sigma–Aldrich, Inc.

In order to eliminate, or at least reduce, the metallic impurities (mainly catalytic metals and amorphous carbon) which can subsequently affect the properties of the nanocomposites and to add some functional groups to facilitate the dispersion, the required amount of CNTs was weighed and then soaked in a 1.0 M nitric acid solution for three hours within ultrasonication bath at 40 °C. Afterward the CNTs were neutralized and washed with deionized (DI) water three times. Every time the CNT conglomerates and sediments were re-dispersed into the DI water and bath-ultrasonicated for 2 min and then centrifuged, using a tabletop high speed centrifuge device, at 13 K
rpm. Finally, the neutralized CNTs were dried in an oven furnace at 70 °C. The dried CNTs were crushed carefully with a ceramic mortar into a fine powder. For each specimen, the required amount of the as-prepared CNTs were weighed and then mixed with 3.0 ml of Acetone followed by 5 min of tip sonication (using a Vibra-Cell VCX 500 tip-sonicator) at 20% amplitude at room temperature. After 1 min of tip-sonication, 1.0 ml Triton X-100 was added to the solution to enhance the dispersion and to prevent the re-aggregation. In order to prevent the CNT–Acetone mixture from conglomeration and sedimentation prior to its usage, the suspension was placed in a bath sonicator and after every 1 min it was tip-sonicated for 10 s. The required amounts of GNPs were also weighed and gradually added directly to the resin while employing high speed dispersion (IKA Ultra-Turrax T-18 basic high speed dispersion unit) under 100% rotation speed. The mixing process was followed up by another 30 min of homogenization inside a water bath at room temperature. After then, the dispersed CNTs were added drop-wise to the as-prepared resin/GNPs suspension and the mix was high-speed dispersed for another 30 min. Finally, to improve the dispersion and distribution, the as-prepared mixture was tip-sonicated for another 30 min in a water bath. Whenever it was needed, disposable wooden sticks were utilized to mechanically mix the ingredients. To ensure proper gelling time, after a number of trials and errors, the proper amounts of curing agent and promoter were weighed and added to the mixture and mechanically stirred followed by one minute homogenization. The CNT/GNP/resin suspension was poured into glass tubes and stored under vacuum in a desiccator for 3 h for proper degassing and to ensure initial curing at room temperature. Finally, the nanocomposite specimens were post-cured in a convention oven for 24 h at 75 °C and were cut into 2.5 mm thick disks using a high precision low-speed diamond saw. Identical processing protocols were carried out for f the mono-filler composites (i.e., CNT/epoxy and GNP/epoxy) specimens.

2.2. Samples characterization

For each composite configuration prepared, a 0.1 mm disk sample was sliced and the morphology of the cryofractured cross section was investigated using a LEO (Zeiss) 1550 field effect scanning electron microscope (FESEM). Several micrographs were generated at different locations on the cross-section under different magnifications.

The electrical conductivities were measured using a 4-point probe station equipped with a Keithley 2001 digital multimeter. The surface resistance was measured at 20 different sites on both sides of each specimen. The averaged value is reported as the electric resistance. The thermal conductivities of the specimens were measured utilizing a Hot disk AB device. For each composite configuration, a Kepton hot-disk probe was sandwiched in-between the flat surfaces of two cleaned disk-shaped specimens. Using a mechanical fixture, the stack was loaded uniformly to ensure proper contact and to minimize the air gap and then the thermal conductivity was measured. For each configuration, the thermal conductivity was averaged over five measurements.

3. Computational study

3.1. Nanofillers aggregation model

Ideally, computational studies treat CNTs and GNPs as perfect straight cylindrical-shaped and disk-shaped particles, respectively, with uniform dimensions. However, in the bulk powder forms, both CNTs and GNPs are typically clustered into large aggregates formed by several nanoparticles entangled together (e.g., CNTs) or stacked on top of each other (e.g., GNPs). Sonication and dispersing processes, to a certain extent, assist in disentangling these aggregates to uniformly distribute/disperse them into the host polymeric matrix. However, even under highly engineered processing protocols, some aggregates are retained in the final nanocomposite. Prolonged homogenization processes could enhance the dispersion of the nanofillers, however this enhancement comes with the caveat of fracturing and deforming the individual particles. Consequently, this will reduce the effective aspect ratios of these nanofillers leading to poor transport properties [25]. Hence, in order to account for these geometric imperfections in the simulations, in the current study the nanofillers are treated as cylindrical aggregates each comprising an average of n individual particle. The number of particles in the aggregate is assumed to vary based on a normal distribution with an average value and a standard deviation estimated from the experimental observations. Furthermore, the aspect ratio of each cylindrical aggregate is selected based on the simple geometric aggregation model defined by

\[ \lambda' = n^{1-3\sigma} \lambda \]  

(1)

In this equation, \( \lambda \) is the nominal aspect ratio of the particles, \( \lambda' \) is the effective aspect ratio of the aggregates and \( σ \) represents the diminution factor that governs the variation of the aspect ratio of the aggregates and it should be estimated from the morphological studies. The parameter \( σ \) is best defined by a distribution with some average value and standard deviation. This equation is simply constructed by assuming that the total volume of the nanofillers is always conserved. Based on the experimental observations, detailed later, and by using image-processing algorithms, the distribution of geometrical dimensions of nanoparticles aggregates were evaluated. Subsequently, the model parameters were selected by fitting the virtual distributions against the experimentally developed ones. In the following computational study for the GNPs the number of particles in each aggregate is selected to follow a normal distribution with \( n = 5 \) and a standard deviation \( σ_n = 3 \) (i.e., aggregates comprising 2–8 GNPs) and the aspect ratio is selected to be normally distributed \( \sigma = 0.1 \) and \( σ = 0.05 \) (i.e., an aggregate possesses reduced diameter due to the deformation and increased thickness due to aggregation). Based on the experimental study, the CNTs form aggregates much easier than the GNPs especially for the high volume fraction configurations (>2.0 wt%). In order to ensure the formation of low aspect ratio aggregates for CNTs, the average number of particles in the aggregate was selected to be \( n = 1000 \) with \( σ_n = 500 \) (i.e., a wide distribution of large aggregates and small ones) and the aspect ratio
was selected to be normally distributed with \( \bar{a} = 0.51 \) and \( \sigma_a = 0.01 \) (i.e., reduced length and increased diameter).

### 3.2. Electrical conductivity model

According to classical Monte Carlo analysis (referred to as MC model onward) [35], the electrical conductivity of the polymer nanocomposites \( \sigma_e \) can be evaluated by

\[
\sigma_e = \sigma_{pre}\exp\left(-\frac{2\delta_v}{a}\right)
\]

(2)

In this equation, \( \varepsilon \) is the tunneling distance, \( \delta_v \) represents the statistically averaged interparticle half distance for which the electrons should tunnel through the polymeric matrix to establish the electrical conductivity and \( \sigma_{pre} \) is a prefactor proportional to the contact conductance. The electrical conductivities of the CNT/epoxy, GNP/epoxy and CNT/GNP/epoxy polymer nanocomposites, with nanofillers loadings concurring with the experimental values, were estimated by this model. For this purpose, each time a random distribution of the nanofiller was generated via Monte Carlo simulation algorithm and the model parameter \( \delta_v \) was calculated and substituted into Eq. (2) to estimate the corresponding effective electrical conductivity. The Monte Carlo simulations, details eliminated here for brevity, were carried out following the technique explained in our previous work [35,37]. For each configuration, the simulations were repeated twenty times to report the average electrical conductivity. In each simulation the tunneling distance was taken to be a constant value \( \varepsilon = 10 \) nm and for the CNT/epoxy and the GNP/epoxy configuration, \( \sigma_{pre} \) was adopted from the values reported in Table 1; for GNPs we used the parallel to the surface value, and for CNTs we utilized the axial value. For the hybrid nanocomposite cases, \( \sigma_{pre} \) corresponding to the CNTs was selected assuming that the weakest element in the percolation network dominates the effective electrical conductivity. Furthermore, in each simulation, the state of the nanofillers agglomeration and geometric imperfections was considered during the particle generation step through the nanofiller’s aggregation model described earlier. For this purpose, the numerical values of the corresponding parameters were estimated from the microscopic observations that will be reported later. Further details about the model and simulation steps can be found elsewhere [35].

### 3.3. Modified strong-contrast (SC) model for thermal conductivity

Per our proposed model [36], the effective thermal conductivity tensor \( \sigma_t \) for the nanocomposite comprises up to three phases (CNTs, GNPs and epoxy), where each phase occupies a volume fraction \( \phi_i (i = 1, 2, 3) \). The thermal conductivity for each of the constituent phases is depicted by isotropic scalar \( \sigma_r \). Hence, the effective conductivity can be evaluated through

\[
\left( \frac{1}{\sigma_r} \sigma_i - 1 \right)^{-1} = \frac{1}{3} \left( \frac{1}{\sum_{i=1}^{3} \phi_i \sigma_i} - 1 \right) I - A_2 - A_3
\]

(3)

where \( \sigma_0 \) is the thermal conductivity of the isotropic reference phase and the second-order terms \( A_2 \) and the third-order terms \( A_3 \) are defined by Eq. (4) and (5) and they epitomize the microstructural information in the solution utilizing one, two and three-point correlation functions \( S_1, S_2^d \) and \( S_3^d \). \( x, b, c = 1, 2, 3 \) scalar phase polarizabilities \( \phi_{0x}, x = 1 \cdots 3 \) and double gradient tensors \( H^{(0)} \). To minimize the estimation error, the reference phase property \( \sigma_0 \) was chosen based on prescribed method [36].

\[
A_2 = \frac{\sigma_0}{\sum_{i=1}^{3} \phi_i \sigma_i} \int \int \int \left\{ \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=1}^{3} \phi_i \phi_j \phi_k S_i^d(1, 2) \right\} d2d2
\]

(4)

\[
A_3 = \frac{3\sigma_0}{\sum_{i=1}^{3} \phi_i \sigma_i} \int \int \int \left\{ \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=1}^{3} \phi_i \phi_j \phi_k S_{ij}^d(1, 2, 3) \right\} \cdot H^{(0)}(1, 2) d2d2d3
\]

(5)

The thermal conductivities of the three systems CNT/epoxy, GNP/epoxy and CNT/GNP/epoxy nanocomposites with nanofiller loadings corresponding to the experimental values were evaluated by this model using the material parameters listed in Table 1. For each nanofiller/epoxy configuration five random nanofiller distributions were generated and the average value of the thermal conductivity was reported. Again, the nanofiller deformation and agglomeration conditions were replicated in the simulation utilizing the nanofiller aggregation model. One and two-point correlation functions \( S_1^d \) and \( S_2^d \) were directly evaluated from the simulated nanoparticle distributions. The three-point correlation functions \( S_3^d \) were approximated from the one and two-point correlation functions following elaborated procedures established elsewhere [39].

### Table 1 – Relevant physical and geometrical properties of the CNTs, GNPs and Epoxy utilized in the simulations gathered from supplier’s datasheet.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Designation</th>
<th>Dimensions</th>
<th>Density [gr cm(^{-3})]</th>
<th>Resistivity [Ω cm]</th>
<th>Thermal conductivity [Wm(^{-1}) K(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs</td>
<td>Short MWCNT</td>
<td>8 nm x (0.5–2) μm</td>
<td>2.1</td>
<td>~1</td>
<td>~1000 a</td>
</tr>
<tr>
<td>GNPs</td>
<td>xGNP-M</td>
<td>5 μm x (6–8) nm</td>
<td>2.2</td>
<td>(5 \times 10^{-5})</td>
<td>3000</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Derakane 411–350</td>
<td>N/A</td>
<td>1.1</td>
<td>(10^{15})</td>
<td>0.2</td>
</tr>
</tbody>
</table>

a Value adopted from the literature [38].
3.4. Estimating the thermal conductivity by finite element analysis

To validate the strong-contrast model’s predictions, the effective thermal conductivities were also evaluated by the finite element method using the commercial finite element code ABAQUS 6.10-EF. For each nanocomposite configuration the generated random microstructure was simulated and meshed with tetrahedral DC3D4 elements by assuming perfect bounding between the particulate inclusions and the epoxy matrix. The FEM solution converged through progressive local and global mesh refinements. For each direction, the boundary conditions were chosen to comprise a constant temperature distributed over the mesh grids on two opposing sides along that direction of the simulation cuboid and the heat equation was solved under steady state conditions. Finally, the effective thermal conductivity was calculated from the temperature difference and the volume averaged heat-flux vector over the entire simulated cuboid. For each specimen, this process was repeated five times with five different representative random microstructures and the average thermal conductivity was reported. Further details about the adopted FEM solution including some samples of the simulation results are provided in the next sections.

4. Results and discussions

4.1. Nanocomposites morphologies

The morphologies of the CNTs and GNP’s embedded in the epoxy matrix were explored via scanning electron microscopy (SEM). Some of the SEM micrographs are shown in Fig. 1. Graphite nanoplatelets can be distinguished by their thin crack-shaped morphology. The low magnification micrograph (Fig. 1a) shows that the GNPs are reasonably distributed within the epoxy matrix. Higher magnification micrographs (Fig. 1b and c) reveal how the GNP particles interlocate to form a local percolation network. This figure also confirms that the GNPs are not perfect disk-shaped nanoparticles; shear-mixing forces (e.g., tip-sonication process) can break them into smaller fragments and distort their shapes.

From Fig. 1d, it can be observed that the utilized mixing technique disperses CNTs well within the specimens with lower loading of CNTs. However, at higher loadings of CNTs (>2.0%wt), the practiced method generated CNTs aggregates. According to Fig. 1e and similar SEM images, the formation of CNT aggregates is more prominent for the composites configuration with high CNTs loadings. From experimental perspective, perfect mixing of samples with high CNT loading (>2.0%wt) is rather a more challenging task. In these specimens, microscale voids and microbubbles are also apparent. Similarly, close inspection of the well-distributed GNPs (Fig. 1f) revealed that usually 2–8 GNPs remained stacked despite the practiced dispersion method.

In Fig. 2a, it can be observed that CNTs play the role of interconnects to form a percolation network between the GNPs planes. For the CNT/GNP/epoxy nanocomposite, CNTs act as conductive flexible pathways spanning in-between the larger high-surface area GNPs. These two species synergistically cooperate to form a hybrid percolation network and, consequently, are expected to enhance the electrical and thermal conductivities of the specimen. The measurements of the diameter and the length of these flexible pathways reveal that even when highly dispersed, a number of CNTs are bundled as nanofilaments. Similarly, Fig. 2b shows that CNT aggregates are also exist in the hybrid nanocomposite configurations with low CNT loadings. However, it is relatively harder to locate them in these specimens. While the formation of such CNT aggregates is not desirable; these aggregates can still contribute to the formation of the percolation network as shown in this figure.

4.2. Electrical conductivity results

The average electrical conductivities of the specimens were measured via the four-point probe method are reported in

![Fig. 1](https://example.com/fig1.jpg) - Random scanning electron microscopy micrographs from different specimens. (a–c) GNPs embedded in the epoxy matrix of 1%wt GNP/epoxy specimens at different magnifications shows uniform distribution, (d) Shows the CNTs distribution in the 1%wt CNT/epoxy specimen, (e) Shows an agglomerated CNT cluster formed in the 5% wt CNT/epoxy specimens, (f) Shows fully exfoliated GNP and an agglomerated GNP cluster consisting 2–8 layers of GNPs stacked on top of each other in a 1.0%wt GNP/epoxy specimen.
The electrical conductivity for GNP/epoxy samples with 1.0–3.0% wt GNP are not reported in this figure since the minimum possible reading by the utilized equipment was $10^{-7}$ S/m which was higher than the conductivity of these specimens. In the current study, the electrical conductivity equivalent to $10^{-7}$ S/m is also selected as the percolation threshold criterion which corresponds to six orders of magnitudes enhancement in the electrical conductivity over that for the base epoxy host matrix.

Fig. 3b depicts the predicted electrical conductivities. By taking the reference threshold for the electrical conductivity to be $10^{-7}$ S/m, the predicted percolation thresholds were found to be 0.6% wt for CNT/epoxy, 0.8% wt for CNT/GNP/epoxy and 1.9% wt for GNP/epoxy configurations, respectively. The corresponding experimentally measured values were 0.6% wt for CNT/epoxy specimens, 0.9% wt for CNT/GNP/epoxy specimens and 3.6% wt for the GNP/epoxy specimens, respectively. It can be observed that the model predictions are in good agreement with the experiments; expect for the GNP/epoxy configuration in which the experimental results are not reliable due to the measurement instrument limitation.

In Fig. 4a, the experimentally measured electrical conductivity of the CNT/epoxy specimens are compared with the model predictions. Upto 2.0% wt CNT, good agreement is observed between the measurements and the model predictions. For higher loadings of CNT, both the experimental measurements and the model capture the saturation of the electrical conductivity, however, the model overestimates the electrical conductivity. This discrepancy between the model predictions and the experimental measurements stems from the incapability of the aggregation model to properly introduce larger aggregate of CNTs into the simulations to reflect the aggregate formation in samples with high CNT loadings. Similarly, Fig. 4b compares the measured electrical conductivity of CNT/GNP/epoxy specimens together with the model predictions. It can be observed that the model predicts the same trend for the electrical conductivity enhancement and the saturation at higher loadings. However, there is still a discrepancy between the predicted values and the experimental measurements. This can be ascribed to the modeling simplifications as well as the assumptions of constant tunneling length and isotropic electrical conductivity for the nanofillers and also to the inherent inaccuracy of the simple geometric nanoparticle aggregation model utilized.

It can be concluded that both the percolation model and experimental measurements suggest that by adding minute amounts of the CNTs (10% compared to GNPs) as the auxiliary conductive phase, the percolation threshold diminishes at least by 50% and the electrical conductivity increases by several orders of magnitudes. This substantial improvement can be attributed primarily to the formation of the highly effective hybrid CNT/GNP networks.
4.3. Thermal conductivity results

The thermal conductivities of the specimens measured by the hot disk method are depicted in Fig. 5a. It can be observed that the CNT/epoxy specimens attain minimal thermal conductivity compared to the two other nanocomposite configurations. The thermal conductivity curve for the CNT nanocomposite specimens reaches a plateau around 1.0% wt CNT with insignificant enhancement in the thermal conductivity. Three sources can contribute to this observation. First, CNTs are more flexible than GNPs and, therefore, are more prone to bending during mixing into the polymer matrix and, in return, their effective aspect ratio is reduced. Second, the formation of the CNT aggregates at higher loadings hinders further enhancement of the thermal conductivity and finally, the high CNT/polymer interface resistance could restrict the effective thermal conductivity of the percolated nanofillers network in these specimens. However, for identical nanofiller weight%, the GNP/epoxy specimens exhibit better thermal conductivity owing to their higher surface area, compared to the CNTs, their more rigid structure and their lower interface resistance.

Finally, it can be observed that the hybrid CNT/GNP/epoxy specimens outperform the two single nanofiller configurations. More than two-fold enhancement in the thermal conductivity was observed for the hybrid nanocomposite configuration comprising 5.0% wt CNT/GNP/epoxy in contrast to the neat epoxy specimen. This enhancement is ascribed to the formation of a more efficient hybrid CNT/GNP networks in these specimens, as observed by SEM micrographs, which reduces the undesirable particle/polymer interfacial resistance effects.

The strong-contrast model predictions of the thermal conductivity of each configuration are represented in Fig. 5b. In agreement with the experimental observation, the hybrid CNT/GNP/epoxy nanocomposite configurations attain the best thermal conductivity compared to the CNT/epoxy and the GNP/epoxy configurations with a single type of nanoinclusions. Similarly, for the assumed nanofiller loadings, the GNP/epoxy specimens are predicted to attain better thermal conductivity in comparison to the CNT/epoxy specimens. The experimental measurements (Fig. 5a) are assertive of these findings.

Both the model and experimental results confirm that for unique filler loadings, the GNP/epoxy nanocomposites exhibit 10–90% higher thermal conductivities in comparison to the CNT/epoxy specimens with identical nanofiller weight percentages. This can be ascribed to the higher surface area

![Fig. 4 – The predicted values for the electrical conductivities of (a) CNT/epoxy specimens and (b) CNT/GNP/epoxy specimens compared to the experimentally measured values. Exp.: experimental measurements, MC: Monte Carlo percolation model predictions.](image)

![Fig. 5 – The thermal conductivity of CNT/epoxy, GNP/epoxy and CNT/GNP/epoxy specimen (a) measured by the hot disk technique and (b) predicted by the modified strong-contrast (SC) model.](image)
and the more robust structure of GNPs compared to CNTs, which is desirable for the phonon transport process. Furthermore, the good agreement between the model and the experimental measurements also implies that there is a lower thermal resistance in the GNP/matrix interface than the CNT/matrix interface which is also reported by other studies[40]. Finally, it can be observed that the hybrid CNT/GNP/epoxy specimens preform up to 15% better than the corresponding GNP/epoxy and up to almost 100% better than their CNT/epoxy counterpart specimens. Nevertheless, it should be emphasized that this synergy effect is more noticeable at lower filler content ranges (<4.0%wt) as increasing the GNP content will increase the GNP/GNP connection density to a degree that suppresses the complementary effect of additive CNTs interconnects in between the GNPs.

The effective thermal conductivities for the different nanocomposite configurations were predicted by both the finite element model and the strong-contrast model and were compared together with the experimental measurements as illustrated in Fig. 6. The models predictions are compared with the experimental measurements of the thermal conductivity of GNP/epoxy specimens in Fig. 6a. Perfect agreement between the model predictions and the experimental measurements can be observed. An acceptable agreement between the SC model prediction and the FEM results can be observed for the GNP/epoxy specimen as well. The predictions of the two models and the experimental measurements of the thermal conductivity for the CNT/epoxy specimens are provided by Fig. 6b. A good agreement is only noticeable for samples with lower loadings of CNTs (<2.0%wt) For CNT/epoxy samples with higher loadings of CNTs, both the strong contrast and the FE models overestimate the thermal conductivity compared to the experimental measurements. In analogy to the electrical conductivity study described earlier, this observation can be attributed to the high tendency of the CNT/epoxy specimens to form large aggregates and the failure of the geometric nanoparticle aggregation model to properly simulate these conditions. Another contributing source for this discrepancy is the high CNT/polymer interfacial resistance and its effect on the performance of the CNT percolation network, which was not considered in both the modified strong-contrast and finite element models (perfect bonding was assumed).

Finally, the predicted values for the thermal conductivity of the hybrid CNT/GNP/epoxy specimens with their corresponding experimentally measured values are depicted in Fig. 6c. A good agreement between the strong-contrast model predictions and the corresponding experimental values can be observed. An acceptable agreement between the SC model prediction and the FEM results is also established.

To provide a better insight into the root differences between the heat conduction mechanisms in different configuration some sample FEM simulation results are provided here. Fig. 7 illustrates finite element predictions of the distribution of the actual heat flux in the simulation cuboids representing two different configurations. Fig. 7a, b are illustrating the

![Fig. 6](image)

Fig. 6 – The predicted values for the thermal conductivities of (a) GNP/epoxy (b) CNT/epoxy and (c) hybrid CNT/GNP/epoxy specimens compared to the experimentally measured values. Exp.: experimental measurements, SC: modified strong-contrast predictions and FEM: finite element predictions.
distribution of the heat flux in a sample simulation cuboid representing hybrid configuration with nanofiller loading of 5%wt GNPs and 0.5%wt CNTs. Fig. 7c, d illustrate corresponding result for the binary configuration with 5%wt CNTs. A comparison between these different configurations provided implies that in the hybrid configuration a more uniform distribution for the heat flux can be expected. However for the binary configuration based on CNTs, the heat flux distribution is characterized with local concentrations and lower uniformity. This observation reveals the physics behind better thermal conductivity of the hybrid configuration.

5. Conclusions

The transport electrical and thermal properties of polymer nanocomposites based on CNTs and GNPs were investigated. A number of polymer nanocomposites comprising 1.0–5.0%wt of CNTs, GNPs and a combination of both were processed and characterized. The electrical and thermal conductivities of the processed specimens were evaluated utilizing newly developed computational models. The computational models estimate the transport properties of each configuration by taking into account the physical properties of its constituents and their state of dispersion and distribution. In an attempt to account for nanofillers agglomeration morphology a geometric model was proposed and implemented in the computations.

The electrical percolation thresholds of each configuration were successfully predicted by the proposed MC percolation model. In agreement with the experimental findings, the MC model predictions suggested that the CNT/epoxy specimens attain lower percolation threshold and higher electrical conductivity than the GNP/epoxy specimens. These findings were attributed to the more facile formation of percolation network compared for CNTs compared to GNPs. However, the experimental study showed that the inevitable formation of agglomeration in high CNT loadings (>2.0%wt) suppresses further enhancement in the electrical conductivity. The MC percolation threshold simulation failed to capture this experimental finding as a consequence of the simplified nanoparticle aggregation model. Both the computational and experimental studies suggest that by incorporating minute amounts of auxiliary CNTs (10% compared to GNPs), the electrical conductivity enhances drastically by several orders of magnitude and the percolation threshold is lowered by 50%. In light of the SEM micrographs, this finding was attributed to the formation of a hybrid CNT/GNP network with naturally enhanced properties.
The strong contrast and finite element models were employed to predict the thermal conductivities of the different nanocomposites. For unique loadings, using the SC model, the CNT/epoxy specimens were observed to exhibit lower thermal conductivity compared to the GNP/epoxy specimens. Finite element simulations confirmed that under ideal interfacial properties, the higher surface area of GNPs compared to CNTs better facilitates phonon transform mechanism. This computational prediction was also substantiated by the experimental measurements and is attributed to the more robust structure of the GNPs and their possible lower particle/matrix interfacial resistance. Furthermore, the experimental measurements and computational models suggested that owing to the formation of the hybrid CNT/GNP network, the hybrid nanocomposites outperform their counterpart monofilier nanocomposites. Finally, this study also confirmed the synergistic nature of the thermal properties of the hybrid CNT/GNP/polymer nanocomposites.

The tools developed in this study provide basis for further development of future multifunctional nanocomposites based on CNTs and GNPs with tailored electrical and thermal properties to oblige many applications in the microelectronics, energy and automotive industries.

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