Synergy effect in hybrid nanocomposites based on carbon nanotubes and graphene nanoplatelets

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Abstract

Hybrid nanocomposites reinforced with a mixture of graphene nanoplatelets (GNPs) and carbon nanotubes (CNTs) have shown improvement in filler dispersion while providing a cost-effective alternative to CNT monofiller composites. Depending on their composition, hybrid composites can exhibit electrical performance superior to either of the constituent monofiller composites due to synergistic effects. In this work, we develop a three-dimensional tunneling-based continuum percolation model for hybrid nanocomposites filled with hardcore particles of elliptical GNPs and cylindrical CNTs. Using Monte Carlo simulations, parametric studies of the filler content, composition and morphology are carried out to analyze the conditions required for synergy in percolation onset and electrical conductivity. Our results suggest that for hybrid systems with well-dispersed fillers, the electrical performance is linked to the number of tunneling junctions per filler inside the percolated network of the nanocomposites. More importantly, hybrid composites filled with specific morphology of GNP and CNT, exhibit synergy in their electrical performance when the monofiller composites of each of those exact fillers have similar percolation onset values. The simulations results are in agreement with relevant experimental data on hybrid nanocomposites.

Keywords: hybrid nanocomposites, percolation, electrical conductivity, Monte Carlo models, carbon nanotubes, graphene nanoplatelets, synergy

(Some figures may appear in colour only in the online journal)
investigated as performant multifunctional materials [10–27]. Even though the cost reduction of the polymer nanocomposites is the main objective, achieving synergistic improvement in the electrical properties of the hybrid CNT–GNP nanocomposites will lead to increased performance. Thus far, the experimental works exhibit unclear trends as of the effect of different parameters of the two fillers on the electrical properties of their hybrid composites, compared to their monofiller composites. Two main trends are observed for the electrical properties of hybrid composites: additive effects [15, 20] and synergistic effects [12, 18, 21]. The additive effect happens when the hybrid composite leads to a performance (e.g. conductivity, percolation threshold) that is better than one of the monofiller, but worse than the second monofiller, similar to the rule of mixtures. By synergy, we imply that the hybrid composite performs better than both monofiller composites, therefore the synergistic effect is more desirable than the additive effect. For example, the 8:2 weight ratio mix of CNT and GNP of specific aspect factors in an epoxy matrix causes synergistic enhancement of electrical percolation and conductivity, i.e. better properties than the weight ratios of 10:0 and 0:10 [25]. This is attributed to GNPs improving the CNT dispersion. In another experimental work, the mix of CNT and GNP in propylene leads only to additive effects in the electrical properties [27]. Increasing the CNT: GNP ratio leads to a monotonous increase in the conductivity between its lowest value at a weight ratio of 0:10 to its highest value at a ratio of 10:0. These reports suggest that the morphology, as well as the relative volume content of the two fillers, affect the likelihood of a synergistic enhancement.

Much work has been done in the literature to extensively study the electrical and piezoresistive performance of CNT and GNP monofiller composites using mostly percolation-based Monte Carlo models [28–36]. In the case of hybrid composites made of CNT and GNP fillers, only a few numerical works studied the electrical performance of hybrid composites [37–42]. Despite the novelty of those works, several modeling-related limitations exist in their formulation. The main limitation comes from the fact that their formulation can only predict the additive effects, or that the synergy improvement in the hybrid composites is observed by comparison only to GNP monofiller composites [37, 39, 42]. However, CNT composites usually have better electrical properties than the GNP ones due to their 1D geometry; hence, synergy should be analyzed with respect to both monofiller composites. Another limitation is the use of softcore (sometimes hardcore) particles without tunneling interactions [38, 41]. While this enables computational efficiency, the models are limited to computing only the percolation threshold and cannot compute the electrical conductivity of the composites. Note that tunneling is considered the primary mechanism for conductivity in nanocomposites [43]. Also, only GNP with circular planar geometry (instead of ellipses) is usually modeled, not considering the unsymmetrical lateral dimensions of GNP after exfoliation. While the aforementioned limitations are modeling-related, the most important feature lacking in the existing numerical works is the fundamental understanding of the mechanisms of electrical conductivity and synergy improvement in hybrid nanocomposites. So far, to the authors’ knowledge, the present work is the first modeling study to examine the synergistic effects in both electrical percolation and conductivity, and the underlying mechanisms that lead to synergy in hybrid CNT–GNP nanocomposites. It is also the first study to evaluate the effect of the type of CNT, its chirality and its intrinsic conductivity on the electrical properties of hybrid nanocomposites.

In this paper, we develop a three-dimensional (3D) Monte Carlo model to examine the microstructures and the mechanisms that lead to synergy in the electrical behavior of CNT–GNP hybrid nanocomposites, beyond the simple additive improvements. The content of both fillers, as well as the planar and transversal aspect ratios of GNP, were parametrically varied to examine the hybrid microstructures that exhibit synergistic enhancement in percolation threshold and conductivity. The effect of aspect ratio, intrinsic conductivity, and chirality of CNT is also studied. We utilize this model to study the parameters related to tunneling junctions that control the hybrid electrical properties, and the mechanisms responsible for the synergistic behavior. We analyze the experimental work from the literature in the context of our model findings.

2. Model formulation

2.1. Three-dimensional modeling of the hybrid composite

We simulated a percolation-based model with the generation of a random distribution of CNTs and GNPs, as shown in figure 1, in a Representative Volume Element (RVE) of size $L_x \times L_y \times L_z$. Every CNT is modeled as a cylinder of diameter $D_{CNT}$ represented by its centerline segment, with midpoint $(x'_c, y'_c, z'_c)$, starting point $(x'_1, y'_1, z'_1)$ and ending point $(x'_2, y'_2, z'_2)$ such that:

$$
\begin{align*}
\begin{bmatrix}
  x'_2 \\
  y'_2 \\
  z'_2 \\
\end{bmatrix} &= \begin{bmatrix}
  x'_c \\
  y'_c \\
  z'_c \\
\end{bmatrix} + l \begin{bmatrix}
  \sin \theta \cos \Omega' \\
  \sin \theta \sin \Omega' \\
  \cos \theta \\
\end{bmatrix} , \quad \text{and} \\
\begin{bmatrix}
  x'_1 \\
  y'_1 \\
  z'_1 \\
\end{bmatrix} &= \begin{bmatrix}
  x'_c \\
  y'_c \\
  z'_c \\
\end{bmatrix} - l \begin{bmatrix}
  \sin \theta \cos \Omega' \\
  \sin \theta \sin \Omega' \\
  \cos \theta \\
\end{bmatrix} ,
\end{align*}
$$

(1)

$$
\begin{align*}
\begin{bmatrix}
  L_x \times \text{rand}_1 \\
  L_y \times \text{rand}_2 \\
  L_z \times \text{rand}_3 \\
\end{bmatrix} , \quad \text{and} \\
\begin{bmatrix}
  \theta' \\
\end{bmatrix} &= \cos^{-1} \left( 1 - 2 \times \text{rand}_4 \right) ,
\end{align*}
$$

(2)

$l$, $\Omega'$ and $\theta'$ are the length, polar angle and azimuthal angle of the ith CNT, respectively. In our previous works [44, 45], we modeled CNTs with a variable length that follows a Weibull distribution, similar to experimental observations of CNT micrographs. In this work, to study the effect of the CNT aspect ratio on the properties of the hybrid nanocomposites, CNTs with fixed length $l$ were used. Every GNP is modeled as an elliptical platelet of thickness $s$, represented by its mid-plane elliptical disk, with center $C_i (x'_c, y'_c, z'_c)$, major axis length $a_i$ and minor axis length $b_i$. 

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such as:

\[
\begin{bmatrix}
    x_i \\
y_i \\
z_i \\
\theta_i \\
\end{bmatrix}
= \begin{bmatrix}
    L_x \times \text{rand}^i_1 \\
    L_y \times \text{rand}^i_2 \\
    L_z \times \text{rand}^i_3 \\
\cos^{-1} \left( 1 - 2 \times \text{rand}^i_4 \right) \\
\end{bmatrix}
\]

and

\[
R = \begin{bmatrix}
\cos \theta^i \cos \Omega^i & -\sin \Omega^i & \sin \theta^i \cos \Omega^i \\
\cos \theta^i \sin \Omega^i & \cos \Omega^i & \sin \theta^i \sin \Omega^i \\
-\sin \theta^i & 0 & \cos \theta^i \\
\end{bmatrix}
\]

\(R\) is the rotation matrix for random orientation, \(T\) is the Cartesian unit vector, and \(\Omega^i\) and \(\theta^i\) are the polar angle and azimuthal angle of the \(j\)th GNP. \text{rand} is a uniformly distributed random number in [0,1].

To obtain realistic microstructures, we prevent fillers’ interpenetration by computing the minimum distance \(d_{\text{min}}\) between either adjacent elliptical disk and line segment, adjacent line segments or adjacent elliptical disks, depending on the fillers in consideration. The algorithm to compute the minimum distance between line segments (CNTs) is relatively simple and easy to implement. However, computing the minimum distance between two elliptical curves is more involved, and can be reduced to the numerical computation of the real-valued roots of a degree 16 polynomial. We have previously derived the minimum distance between two adjacent elliptical disks (GNPs) and the distance between adjacent elliptical disk and line segment (GNP and CNT) in [40]. These require additional calculations, compared to the case of two elliptical cures as shown in supplementary data (stacks.iop.org/Nano/31/255704/mmedia). We have interpenetration between fillers if: (a) \(d_{\text{min}} < d_{\text{vdw}} + t\) in case of adjacent GNP, (b) \(d_{\text{min}} < d_{\text{vdw}} + D_{\text{CNT}}\) for adjacent CNTs and (c) \(d_{\text{min}} < d_{\text{vdw}} + \frac{t}{2} + \frac{D_{\text{CNT}}}{2}\) in case of adjacent GNP and CNT. In the case of interpenetration, the new particle is discarded and another one is generated until there is no interpenetration. \(d_{\text{min}}\) is stored as the tunneling distance between the two fillers, if \(d_{\text{min}} \leq d_{\text{vdw}}\). \(d_{\text{vdw}}\) is the tunneling cutoff distance and is assumed to be 2.6 nm. For faster computation, in the case of adjacent CNTs, the RVE is partitioned into uniform grids. Every CNT is assigned to all the bins it intersects. Only the CNTs inside the assigned bins of the newly generated CNT or the bins directly adjacent to those are checked for distance calculation. Bins of size five times smaller than the CNT length are used, following [46]. We implemented periodic boundary condition (PBC) on all sides of the RVE when part of a filler is outside of the RVE. PBC for CNT in 3D is relatively simple and similar to the procedure in 2D [29]. PBC in 3D for elliptical GNP filler requires additional steps compared to linear or circular particles. If an elliptical particle intersects one (or two) boundaries, one (or two) additional elliptical particles are compensated back on the opposite boundaries, as shown in figure 2(a) and (b). If the particle intersects two boundaries with their common edge, three particles are compensated, as shown in figure 2(c). If the particle intersects boundaries, with one of their common edges, four particles are compensated. If it intersects three boundaries, with two of their common edges, five particles are compensated. In the case of three boundaries with their common three edges, six particles are compensated as shown in figure 2(d). Figure 3 shows nanocomposites at their percolation onset, filled with different amounts of CNT and GNP, generated using the current modeling approach.

2.2. Electrical percolation and conductivity modeling for hybrid microstructures

From section 2.1, we obtained hardcore hybrid microstructures with all the tunneling distances between adjacent fillers computed. Fillers with an inter-particle distance less or equal
to the tunneling cutoff distance, $d_{\text{cutoff}}$ are assumed electrically connected and form a cluster. When a cluster of connected fillers bridges two electrodes of the RVE (planes $z = 0$ and $z = L_z$), we have percolation in the RVE, and the conductance of the nanocomposites is equal to that of the cluster. The percolation of the composite is evaluated using the percolation probability, which is the probability that there is at least one conductive path in the RVE spanning the two electrodes. It is defined as $P = \frac{n_p}{N}$ where $n_p$ is the number of microstructures with the existence of at least one conductive path in a total of $N$ microstructures [29]. The percolation threshold or onset ($V_{50}$) corresponds to the total volume fraction of fillers ($V_{T} = V_{\text{CNT}} + V_{\text{GNP}}$) when $P = 50\%$ [29]. $V_{\text{CNT}}$ and $V_{\text{GNP}}$ are respectively the volume fraction of CNT and GNP inside the nanocomposites. Additionally, we also compute the volume fraction ($V_{100}$), which is the minimum volume fraction of fillers needed to have percolation in all $N$ microstructures, when $P = 100\%$. To compute the conductivity of the RVE, the tunneling distances, $d_{\text{min}}$ between fillers are first transformed into resistors of resistance (tunneling resistance) proportional to $d_{\text{min}}$. Assuming a square tunneling barrier height, $\lambda = 0.5 \text{eV}$, the tunneling resistance is approximated in [47] by:

$$R_t = \frac{\hbar^2 d}{4e^2 \sqrt{2m\lambda}} \exp \left( \frac{4\pi d}{h} \sqrt{2m\lambda} \right)$$

where $\hbar$ is Planck’s constant, $d$ is the tunneling distance, $e$ is the quantum of electricity, $m$ is the mass of an electron and $A$ is the cross-section area of the tunnel. In addition, the fillers inside the percolated network are transformed into resistors of resistance (intrinsic resistance) proportional to their size and inversely proportional to their intrinsic conductivity. The calculations for intrinsic resistance $R_{\text{int}}$ for CNT and GNP are provided elsewhere [44]. Kirchhoff’s current and Ohm’s laws are used with the incomplete Cholesky conjugate gradient method [48] to calculate the resistance of the RVE.

### 3. Results

Carbon nanotubes of constant length $L_{\text{CNT}} = 100 \text{nm}$ and diameter $D_{\text{CNT}} = 10 \text{nm}$ are modeled as multi-walled CNTs (MWCNT) unless stated otherwise in a cubic RVE of length $L_{\text{RVE}} = 1000 \text{nm}$ for all the nanocomposites studied. GNP modeled as an elliptical cylinder with major axis length kept constant $a = 100 \text{ nm}$ is used as second filler. GNPs of different morphology are simulated, controlling the planar aspect ratio ($\text{AR}_p$) and the transversal aspect ratio ($\text{AR}_t$) such that: $\text{AR}_p = a/b$ and $\text{AR}_t = a/t$, where $b$ and $t$ are respectively the minor axis and the thickness of the GNP. $\text{AR}_p = 1$ results in circular GNPs with the diameter equal to $a = b$. The following procedure is adopted for this section. First, a morphology of GNP is chosen by either fixing $\text{AR}_p$ or $\text{AR}_t$. The chosen GNP is then mixed each time with CNT of different CNT volume ratios ($X = V_{\text{CNT}}/V_{T}$) to obtain eleven different nanocomposites, each corresponding to a value of $X = 0, 0.1, 0.2, \ldots, 1$. The first nanocomposite is filled with only GNP, the second nanocomposite is filled with 10% vol. of CNT and 90% vol. of GNP and so forth. $X = 1$ corresponds to CNT monofiller composite. For each of the 11 nanocomposites, we determine their percolation threshold $V_{50}$ and the minimum filler content for 100% percolation probability $V_{100}$. The percolation of the
hybrid nanocomposites made with the GNP morphology is the curve connecting the 11 data points of V_{50}. Next, the electrical conductivity of each of the 11 nanocomposites is computed at the same filler content, to allow for comparison. Hence, we find V_{100Max}, which is the maximum of the 11 values of V_{100} and define V_C = 1.03 \times V_{100Max}. The conductivity of each of the 11 nanocomposites is computed at the same filler content V_C. Finally, the total number of tunneling junctions between adjacent fillers in each of the 11 nanocomposites is computed at the same filler content V_C and plotted. The same procedure is followed for each morphology of GNP studied to obtain three 11-data-points curves (for percolation threshold, conductivity and number of tunneling junctions) for their hybrid composites.

We use Monte Carlo simulations based on the model described in section 2 to generate fillers with a random position and orientation and compute the effective value of the properties of the nanocomposites (percolation threshold and electrical conductivity) following the procedure described above. We reduce the statistical variation of the measured properties by averaging over 70 randomized microstructures. 70 Monte Carlo sample microstructures were used due to computational limitations since the generation of each hardcore hybrid microstructure takes usually at least between 4 to 7 d.

3.1. Effect of GNP transversal aspect ratio on electrical properties of hybrid microstructures

The exfoliation of graphite during the nanocomposite’s fabrication usually leads to a reduction of both the thickness and the lateral size of graphite. In this section, we fixed AR_p = 1 to model circular GNPs with a fixed diameter a = b = 100 nm. Only the transversal aspect ratio AR_t is varied from 15 to 34. For each value of AR_t, the percolation threshold, conductivity, and the number of tunneling junctions at all hybrid compositions (all values of X) are computed as described above. The percolation threshold curves for each value of AR_t are plotted and compared in figure 4(a) while the conductivity curves are compared in figure 4(b).

Some of these curves in figure 4 vary monotonically with respect to X, reflecting the additive effects while others exhibit a critical point, showing the synergy effects. Figure 4(a) shows that the hybrid composites with GNP of AR_t values 15, 17, and 20 exhibit additive effect (dashed lines) in percolation onset. This implies that the monofiller composite with only CNT (X = 1) has a lower percolation threshold compared to all the hybrid composites with GNPs of these aspect ratios. For all the other values of AR_t, the hybrid composites exhibit synergistic improvement (represented by solid lines) in percolation onset at some values of X. We see that increasing AR_t helps transition from hybrids with only additive effects in percolation to hybrids with synergistic effects. In addition, increasing AR_t too much seems to lead back to hybrids with additive effects, as shown in the plot for AR_t = 34 in figure 4(a).

Increasing AR_t similarly affects the presence of synergy in the conductivity of the hybrid composites, as shown in figure 4(b). In general, increasing AR_t of the GNP systematically leads to lower values of percolation. Note that in figure 4(b), for a chosen AR_t, conductivity is computed at the same filler content V_C. However, V_C is not the same for all the values of AR_t. Hence, a comparison between the conductivity curves of two different AR_t is not effective if their V_C is different. However, since the conductivity for the hybrids with GNP of AR_t = 27, 29, 32, 34 are computed at the same V_C, a comparison is possible. Comparing the four conductivity curves for AR_t = 27, 29, 32, 34, we see that increasing the AR_t of GNPs in the hybrid composites increases the conductivity and lowers the percolation threshold for all values of X. In addition, synergy in the percolation threshold usually leads to synergy in electrical conductivity.

Experimental studies on CNT–GNP hybrid composites have explained both synergistic and additive enhancements by the improved state of CNT dispersion in the presence of GNPs [25] and the ability of CNTs to easily bridge the distance...
between GNPs [27], leading to an easier formation of the percolated network in the composites. However, numerical studies have been unable to capture the microstructure’s parameters that control the performance of hybrid composites thus far. It is generally accepted, based on numerical simulations results, that the total number of tunneling junctions between fillers is a primary indicator of the electrical performance of CNT and GNP monofiller composites [28]. A higher number of junctions leads to better electrical properties. Hence, for the first time, we examined four different parameters related to the number of tunneling junctions in all the hybrid microstructures to understand which one of the parameters controls the electrical performance. Figures 5(a)–(d) show the plots respectively for (a) the number of tunneling junctions (between the fillers) in the entire microstructure (Nt), (b) the number of tunneling junctions only in the percolated network in the microstructure (Ntp), (c) the number of tunneling junctions per filler (ratio), in the entire microstructure (Rt), and (d) the number of tunneling junctions per filler only in the percolated network in the RVE, Rtp. We see that Rtp in figure 5(d) is the only microstructure’s parameter that correlates with the electrical performance of the hybrid composites because it shows the same trend as the curves for conductivity in figure 4(b), for GNP with ARt = 17 and 25. Figure 5(e) shows the plots of Rtp for all the ARt values, computed at their respective filler content Vc. Increasing ARt leads to the improvement of Rtp and the transition between additive and synergistic effects in Rtp, like what was observed for percolation and conductivity.

3.2. Effect of GNP planar aspect ratio on electrical properties of hybrid microstructures

In this section, to characterize the effect of the lateral dimensions of GNPs, we fix the value of ARt and vary the planar aspect ratio (ARp) of GNP from 1 to 2, 3, and 4. This changes the planar dimensions of the GNP from a circle to different ellipses, by varying the minor axis b, while the thickness t and major axis (a = 100 nm) are kept constant. This allows us to model GNPs with radially unsymmetrical lateral dimensions. The same procedure in section 3.1 is followed here to examine the effect of ARp on the electrical performance of the hybrid composites. We start with hybrids made of GNP ARt = 25, which exhibit synergy in percolation and conductivity in figure 4. Figure 6 shows that increasing ARp systematically decreases the percolation threshold and increases the conductivity, as well as Rtp. The percolation threshold of the GNP nanocomposites (X = 0) decreases from 10.80 to 8.73 vol.% when ARp is varied from 1 to 4. A two order of magnitude increase (from 8.20 × 10−5 S m−1 to 1.5 × 10−2 S m−1) is observed in the conductivity of GNP nanocomposites (X = 0) when ARp is varied from 1 to 4. While most of the hybrid composites with GNP ARp = 1 exhibit synergy in percolation, all of them show synergy with GNP ARp = 2. Increasing ARp more to 3 and then 4 leads to fewer hybrids (fewer values of X) that exhibit synergy. Similar trends are observed in conductivity and Rtp values.

In figure 7, we study hybrids made of GNP ARt = 17, which exhibit additive effects in percolation and conductivity (in figure 4), to examine the effect of varying ARp from 1 to 4 with an increment of 1. As in the case of GNP ARt = 25, increasing ARp from 1 to 4 leads to the decrease in percolation threshold and the increase in conductivity. However, in the case of ARt = 17, none of the hybrid composites with GNP ARp = 1 shows synergy in either percolation, conductivity, or Rtp. Increasing ARp to 2 and 3 still does not lead to synergy in any of the hybrids (all values of X). Only an increase of ARp to 4, finally leads to synergy in percolation, conductivity, and Rtp in many of the hybrid microstructures.
Compiling the results in figures 4, 6 and 7, we can conclude that decreasing the values of the GNP aspect ratios (AR_t and AR_p) does not directly lead to synergy. Only values of GNP aspect ratio in a specific range (e.g. AR_t = 22, 25, 27, 29 and 32 in figure 4(a)), lead to hybrid with synergistic improvement. When we look at the percolation results for GNP aspect ratio in that range, we see that synergy happens only if the percolation threshold value of the chosen GNP in its monofiller composite (X = 0) is very close to the one of the CNT composite (X = 1). The closer the percolation threshold values of the two monofiller composites (X = 0 and X = 1) are, the more hybrid composites (more values of X) exhibit synergy (see AR_t = 25 and AR_p = 2 in figure 6). Hence, we can confirm that the synergy effect in the electrical properties of hybrid composites is directly related to the closeness of the percolation threshold values of their GNP monofiller and CNT monofiller composites.

3.3. Effect of chirality of CNT and CNT intrinsic conductivity on electrical properties of hybrid microstructures

The results presented so far are computed using CNTs with intrinsic conductivity \( \sigma_{CNT} = 10^4 \, S/m \) as MWCNTs since they are a cheaper alternative to single-walled CNTs (SWCNTs) and hence lead to cost-saving in addition to the synergistic enhancement when combined to GNP. In this section, we are studying how the intrinsic conductivity of CNT affects the conductivity as well as the presence of synergy and additive effects in the conductivity of hybrid nanocomposites. We use \( \sigma_{CNT} = 2 \times 10^7 \, S/m \) for armchair SWCNTs and \( \sigma_{CNT} = 10 \, S/m \) for zig-zag SWCNTs, following the work done in [49]. In this section, only the intrinsic conductivity value of the CNT is changed. Changing the diameter from MWCNT (10 nm) to SWCNTs (1–2 nm) would increase the aspect ratio of CNTs (decrease the percolation threshold) as...
studied in section 3.4. Thus, in this section, the percolation threshold values are not changed, only the conductivity of the nanocomposites is then studied. Figure 8(a) shows the conductivity of CNT monofiller nanocomposites when the intrinsic conductivity of CNT is varied. We see that for low content of CNT (<12%) the conductivity of the composites is the same. With a higher content of CNT fillers, the conductivity of both MWCNT and armchair SWCNT composites becomes much higher than that of zig-zag SWCNT. The conductivity of MWCNT and armchair SWCNT composites remains very similar up to a CNT content of 16% even though the conductivity of armchair SWCNT composites is slightly higher than the one of MWCNT as shown in table 1. We can predict from table 1 that increasing the content of CNT will lead to the conductivity of armchair SWCNT composites being much higher than the one for MWCNT composites. This is explained in [49, 50] by the fact that at low content of CNT, connectivity happens mainly due to tunneling effects because the fillers are apart and only a few of them are present in the percolated network; hence the conductivity of the composites is dominated by tunneling resistance. At high content of CNTs, the fillers are closer to each other and the percolated network is filled with CNTs, hence the conductivity of the composites is dominated by the CNT intrinsic resistance.

However, the intrinsic conductivity of CNT does not affect the presence of synergy or additive effects in the hybrid composites. This proves as suggested in the previous section that synergy in hybrid composites is directly linked to the improved connectivity between the fillers in the hybrid microstructures.

### 3.4. Effect of CNT morphology on electrical properties of hybrid microstructures

The results presented so far are computed using CNTs (L
\_\text{CNT} = 100\text{nm}) of aspect ratio AR = 10 as primary fillers, leading to the use of GNPs with transversal aspect ratio, AR, between 15 to 50 in order to have hybrid composites exhibiting synergistic electrical properties. While CNT and GNP fillers with higher aspect ratios ~100 to 1 000 are commonly used experimentally for nanocomposites, several works also exist with fillers of low aspect ratio ~10 to 50 [51–59]. In general, conductive nanocomposites fabricated using inkjet printing rely on CNT and GNP fillers of low aspect ratio to avoid clogging the printer nozzle [52, 56, 58, 60]. In addition short CNTs (low aspect ratio) are increasingly used to reduce the
extent of agglomeration in the nanocomposites [59]. The results presented so far correspond to such situations. In this section, we examine the effect of using CNTs with higher aspect ratios (by decreasing the diameter $D_{\text{CNT}}$) on the electrical properties of the hybrid nanocomposites, mainly in term of the morphology of GNP fillers needed for synergistic behavior. Figures 9 and 10 respectively show hybrid nanocomposites made of CNTs of $AR = 50$ ($D_{\text{CNT}} = 2\,\text{nm}$) and $AR = 100$ ($D_{\text{CNT}} = 1\,\text{nm}$) as primary fillers. The CNTs fillers can also be assumed to be SWCNT which diameter is usually about 1–2 nm [49]. We can see that for higher AR of CNTs, GNP fillers with higher AR (compared to the case of CNTs with AR = 10) are needed to obtain hybrid composites exhibiting synergy in their electrical properties. While mixing GNPs of AR$_t$ = 22–32 to CNT of AR = 10 leads to hybrids with synergy in figure 4, GNPs of AR$_t$ = 350–450 and GNPs of AR$_t$ = 1000–1600 are needed respectively for CNT AR = 50 and CNT AR = 100.

In addition, the percolation curves for all hybrids that exhibit synergy decrease when the aspect ratio of CNT filler increases. Specifically, percolation threshold values of hybrids with synergy decrease from a range of 8.5%–12%, for CNT AR = 10 (figure 4(a)) to a range of 0.9–1.2%, for CNT AR = 50 (figure 9(a)) and finally to a range of 0.27%–0.53%, for CNT AR = 100 (figure 10(a)). As explained in the previous sections, CNT and GNP fillers with close values of percolation threshold in their respective monofiller composites lead to synergy in their hybrid composites. Hence, a higher aspect ratio of CNTs (with lower percolation threshold in their monofiller composites) will require a much higher AR$_t$ of GNPs with similarly low percolation threshold. This information in the context of the comparison between SWCNT
Figure 11. Synergy effect in (a) percolation threshold and (b) conductivity based on difference ratio between percolation threshold of GNP and CNT nanocomposites. Contour plot showing synergy zone.

Figure 12. Improvement in (a) percolation threshold and (b) conductivity in hybrid nanocomposites due to synergy, using filled contour plot with isolines.

and MWCNT means that using CNT fillers of same length, SWCNT will require higher AR of GNP fillers to achieve synergy in the hybrid composites compared to MWCNTs. In addition, SWCNTs will lead to hybrids with lower percolation threshold and much higher conductivity. Hybrids with arm-chair SWCNTs will be more conductive than the ones with zig-zag SWCNTs.

There are some numerical issues related to the modeling of high aspect ratio fillers. In general, the relative size of the RVE to the length dimension of filler (major axis of elliptical cylinder for GNP and length of cylinder for CNT) is a key input for percolation onset. In multi-filler composites, this ratio (RVE size-to-filler length) should be similar for both GNP and CNT fillers in order to accurately compare the percolation properties of the two fillers. This has been shown in [38] and has been observed in this study as well. We have also shown that percolation onset of the two fillers in their monofiller composites should be similar to achieve synergy in the hybrids. When combined with the limitation on the ratio of RVE size-to-filler length, this imposes certain limitations on the GNP dimensions. Since high aspect ratio of CNT requires a much higher aspect ratio (ARₚ) of GNP to obtain synergy in hybrid composites, the thickness of GNP in the simulations could become unphysically low. Within the computational limitations, this could be addressed by non-dimensionalizing the system (e.g. [38]), or by using low aspect ratio fillers with equal particles’ length [37, 38, 42, 61].

4. Discussion

All the experimental studies on the electrical properties of CNT-GNP hybrid nanocomposites indicate that the relative content of each of the fillers in the hybrid (X), controls the percolation and electrical conductivity of the hybrid nanocomposites. Some observed a synergistic improvement in percolation and/or in conductivity at some specific values of X [13, 14, 25], while others only experienced an additive effect [11, 21, 24, 27]. Our numerical model is able to predict those two effects in percolation and conductivity for CNT-GNP hybrid nanocomposites, by varying the CNT volume ratio (X) and also the morphology (planar and transversal aspect ratios) of the GNP filler. We show that increasing either the planar or transversal aspect ratio of the GNP filler in the hybrids leads to a decrease in the percolation threshold and an increase in the conductivity of all the hybrid composite compositions (all values of X).
Nonetheless, we show that no direct correlation exists between the variation of any of the GNP aspect ratios and the existence of synergy or additive effects in the hybrid composites. We also show that the type of CNTs used, specified by the CNT aspect ratio, its chirality, and its intrinsic conductivity also affects the electrical properties of the hybrid nanocomposites. While the aspect ratio of CNTs (also the choice of MWCNT or SWCNT) affects the percolation threshold values as well as the morphology of GNP required to achieve synergy, we show that the CNT intrinsic conductivity (also the chirality of SWCNT) only affect the electrical conductivity of the hybrids and does not affect the presence of synergy.

To understand the property of the nanocomposites that creates synergy in the hybrids, we analyzed all of the percolation and conductivity obtained in this study in figure 11. To do so, we first choose a GNP morphology and compute the difference ratio between the percolation values of its GNP and CNT monofiller composites, \( \frac{P_{\text{GNP}} - P_{\text{CNT}}}{P_{\text{CNT}}} \). This represents the y-coordinate in figure 11 for the hybrids with that GNP morphology. Next, for each of the 9 hybrid composites \((X = 0.1, 0.2, \ldots, 0.9)\), we have either synergy (filled marker) or additive effects (empty marker). Figures 11(a) and (b) analyze the synergy or additive effects in percolation threshold and conductivity using the data from varying both the GNP planar (triangle marker) and transversal (square marker) aspect ratios. For example, for hybrid composites with circular GNPs with \( R_t = 17 \), the percolation values, \( V_{50} \) of CNT and GNP nanocomposites are \( P_{\text{CNT}} = 10.35 \text{ vol.\%} \) and \( P_{\text{GNP}} = 14.40 \text{ vol.\%} \), as shown in figure 4(a). The y-coordinate for the 9 hybrids \((X = 0.1, 0.2, \ldots, 0.9)\) made of that GNP is \( \frac{P_{\text{GNP}} - P_{\text{CNT}}}{P_{\text{CNT}}} = 38\% \). Figure 11 shows that we have additive effects (empty square markers), respectively for percolation (figure 11(a)) and conductivity (figure 11(b)) for the hybrid composites with GNP of \( R_t = 17 \).

Additionally, we compute a synergy contour that encompasses all the instances of synergy in percolation and conductivity, respectively, in figures 12(a) and (b). It shows that when the percolation threshold of the GNP monofiller composite \((X = 0)\) is close (±20\%) to that of the CNT monofiller composite \((X = 1)\), the hybrids made of those two fillers will likely achieve synergistic improvement. In addition, the closer the values of the two percolation onsets are, the more hybrid compositions (more \( X \)) will exhibit synergy.

Figures 12(a) and (b) show the improvement in percolation and conductivity obtained from the hybrid composites examined in this work. To obtain the numerical value for the improvement in conductivity, the conductivity of each hybrid at a given CNT volume ratio \((X)\) is compared to the highest of the conductivity values between monofiller CNT \((X = 1)\) and monofiller GNP \((X = 0)\) composites. For the improvement in percolation, the percolation value of each hybrid is compared to the lowest of the percolation threshold values between monofiller CNT and GNP composites. An improvement of 800\% in conductivity was obtained through synergy, as shown in figure 12(b).

Figure 13 shows a comparison of the data from our numerical simulations and several experimental works. We see that indeed synergy happens in hybrid nanocomposites filled with GNP and CNT fillers, if and only if, both fillers have percolation threshold values very close to each other in their monofiller composites. When their percolation threshold values are far apart, only the additive effect is observed. To the authors’ knowledge, this is the first time that the synergy effect in hybrid composites is linked to the percolation threshold of their monofiller composites. Note that some of the
experimental works used molecular weight fraction instead of volume fraction. For comparison sake, their results are converted to volume fraction, assuming that the density of CNT and GNP is 2.1 g cm$^{-3}$. In addition, some of the experimental studies have explained the improvement of electrical performance in CNT-GNP hybrid composites by the improved state of CNT dispersion in the presence of GNPs [25]. We have studied the effect of agglomeration on the electrical and piezoresistive performance of both monofiller and hybrid composites elsewhere [45]. Our present numerical formulation considers the fillers to be uniformly dispersed in the composites. However, using this formulation, we were able to isolate the microstructural mechanism which leads to synergy effects in hybrid nanocomposites. We show in figure 5 that the number of tunneling junctions per filler, in the percolated network, $R_p$ controls the electrical performance of the hybrid composites. Further, we also identify that synergy occurs in hybrid composites only for compositions where the monofiller composites have similar percolation thresholds.

5. Conclusions

In this paper, we developed a three-dimensional (3D) Monte Carlo model to understand the mechanisms and microstructural features that control the electrical behavior of hybrid nanocomposites filled with CNT and GNP, and potentially lead to a synergistic effect. The primary conclusions of the study are as follows: (a) Increasing either the planar or transversal aspect ratio of the GNP filler leads to the improvement of both percolation threshold and electrical conductivity of all the hybrid composites. (b) When the percolation threshold of the GNP fillers in its monofiller composite is within 20% of the percolation threshold of the CNT fillers in its monofiller composite, the hybrid composites made of those two specific fillers achieve synergistic improvement in electrical properties. Our model suggests an improvement in electrical conductivity as high as 800% in hybrid nanocomposites due to the synergy achieved using the above combination of fillers. (c) Increasing the aspect ratio of CNT leads to the increase of the planar aspect ratio of the GNP fillers required to achieve synergy and also leads to hybrids with lower percolation and higher conductivity. (d) Using CNT with a higher value of intrinsic conductivity increases the conductivity of the hybrids but does not affect the presence of synergy or additive effects. (e) Using SWCNT instead of MWCNT will require GNPs with a higher planar aspect ratio in order to achieve synergy in the hybrid composites. It will also lead to hybrids with better electrical properties. A change in the chirality of SWCNT will only affect the conductivity of the hybrid composites without altering the presence of synergy or additive effects. (f) A review of past experimental data matches our numerical results and confirms the correlation between the closeness of the percolation threshold values of the two monofiller nanocomposites and the synergy effects in the corresponding hybrid. (g) We find that a key microstructural parameter, that controls the electrical performance of the hybrid composites is the number of tunneling junctions per filler, in the percolated network. Improvement or synergy of that parameter leads to an improvement or synergy in percolation threshold and electrical conductivity in the hybrid nanocomposites.

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Conflict of interest

The authors declare that they have no conflict of interest.

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