Percolation Behavior of Electrically Conductive Graphene Nanoplatelets/Polymer Nanocomposites: Theory and Experiment

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Percolation behavior of graphene nanoplatelet (GNP) filled electrically conductive nanocomposites of polymers was studied theoretically and experimentally. A modified power law based percolation theory was formulated to include particulate geometry and temperature dependence. Pristine and vinyl acetate/butyl acrylate functionalized GNPs were synthesized for further usage in preparation of poly(methyl methacrylate) (PMMA) nanocomposites via in situ polymerization. Structural characterization of the samples showed their unique quality. Best values of percolation threshold and maximum conductivity were found to be 0.3 vol.% and $10^{-1}$ S/cm, respectively. Modified power law allowing one to predict the percolation by knowing only aspect ratio of GNPs was successfully described our graphene-polymer model system as well as wide range of literature collected data. Our results could serve as a design tool in graphite nanofiller based conductive composites.

Keywords Graphene nanoplatelets, polymer nanocomposites, percolation theory, electrical properties

1. Introduction

Graphene, as a real 2D material in the form of sp² carbon, has “wonderful” features (1) for numerous applications. Electronic properties are especially distinguished with enormous electron mobility at room temperature up to (1) and massless fluid-like fermions with relativistic velocities ($c/300$) (2). In combination with unique mechanical, thermal and chemical properties, amazing electronic behavior of graphene offers great potential for vast variety of applications such as transparent and/or flexible electronics, energy devices, light emitting diodes, electromagnetic interference shielding, structural health monitoring, lightning protection and so forth. Graphene is used in all above applications as a hybrid in a polymer matrix and in this respect it is essential to understand the properties of electrically conductive graphene-polymer nanocomposites. Although research on the electrical properties of graphite nanostructure filled polymers began more than a decade ago (3–7) they have been mostly ignored in graphene literature. Recently, interest in graphene based electrically conductive nanocomposites has significantly grown (8–16). Unfortunately, most of them used empirical approaches and theoretical knowledge of conduction mechanism is still not clear.
Graphene-polymer hybrids can be identified as semi-permeable heterogeneous materials whose one of the most fundamental properties of their transport processes is the percolation which is a nonlinear permeability dependence on the system composition/configuration. Electrical/thermal conductivity for electrically/thermally conducting composites, permeability for porous materials and viscosity of colloids (17–20) and even dynamics of complex networks (21) are all well defined by the percolation theory. Clearly, resolving the percolation behavior of graphene-polymer nanocomposites will elucidate the design problems of graphene based organic electronics and materials.

This paper is concerned with the percolation theory of graphene based polymer nanocomposites. In section 2, traditional power law was modified to incorporate geometrical and electrical properties of graphene. This modified law was tested and validated with extensive literature data from previously published papers and showed superior success in the prediction of percolation threshold, critical exponent and temperature dependence. We also fabricated PMMA nanocomposites using GNP, that is, multilayer graphene which is a promising, low-cost and high quality industrial nanomaterial in comparison to monolayer graphene. In order to seek for properties of GNP and GNP/PMMA nanocomposites, morphological characterization were briefly presented and discussed. In the last section, we advanced model validation attempts by DC electrical conductivity measurements on our GNP/PMMA nanocomposite samples with incremental GNP loading and varying temperature. The suggested model was able to fit our experimental percolation data in both nanofiller content and temperature dependences.

2. Theoretical Model

Electrical conductivity of an insulating media containing conducting inclusions (See Figure 1) is described by the percolation theory in the vicinity of insulator-conductor transition. Percolation theory (17) proposes that below a critical concentration conducting inclusions are individually isolated in the insulating matrix. As the concentration of inclusions increases, connection probability of inclusions also increases until a network construction of the particles appears corresponding to a sharp change in the conductivity of the system from insulator to semi-metal conductor. During this process, actual physics of the conduction is determined by composition of the insulator/conductor system (18). Electron transport in granular metals, for instance, evolves on the contacting particles. However, transport in a polymer filled with conducting particles is due to the electron

Figure 1. Schematically simulated visualization of particle distribution in a graphene-polymer nanocomposite. 3D random orientation of graphenes embedded in polymer volume (a), agglomeration of graphenes (b) and graph/network representation of the actual nanocomposite (c) (color figure available online).
hopping/tunneling across the inter-particle gaps on the network. Beyond the critical concentration, so-called “percolation threshold,” all the particles interface with each other and only a thin polymer layer of a few nm separates them which enable the quantum mechanical tunneling. Further concentrating the particle network will cause saturation and conductivity achieves an upper limit which is quite below the conductivity of pure inclusions. Percolation mechanism can be expressed pretty well as a power law (17,19):

\[ \sigma = \sigma_e (\phi - \phi_c)^s ; \; \phi > \phi_c \]  

(1)

where \( \sigma \) is the conductivity of bulk resultant material, \( \sigma_e \) is the effective conductivity of inclusion, \( \phi \) is the volume fraction of inclusion, \( \phi_c \) is the volume fraction at percolation threshold and \( s \) is the critical exponent. Although \( \phi_c \) is a function of inclusion/matrix topology, magnitude of the exponent \( s \) is generally accepted as an idealized universal value of \( s_u = 1.6–2.0 \) (17, 18) or \( s \approx 1.1–1.3 \) for 2D particle distribution and \( s \approx 1.6–2.0 \) for 3D distribution (19). However, instead of this theoretical conclusion, non-universal critical exponent \( s > 2 \) (5,7), even up to \( s = 4 – 5 \) (14,18) can be frequently found in literature.

2.1. Percolation Threshold

Equation (1) has been widely addressed in literature (5,7,14,22–28) to fit the experimental nanocomposite electrical conductivity data as a function of GNP content without a clarification for physical background of the model. In recent attempts, some non-traditional methods were chosen to develop different perspectives on percolation of graphene-inpolymer systems such as McLachlan’s generalized effective-medium (GEM) model (11, 29), and \( \phi_c^{\text{effective}} - \phi_c \propto L^{-1/\delta} \) (\( L \): system size; \( \delta \): system size critical exponent) scaling relation (14,30). But, elucidation of the physical insights into the percolation theory of GNP-polymer nanocomposites needs a more fundamental investigation based on real life parameters rather than abstract concepts. Particularly, design of conductive nanocomposites should be accomplished with minimum available information about their components, e.g. geometry of nanoparticles. In the case of GNPs, geometry is defined by their aspect ratio \( \alpha = D/t \), where \( D \) diameter (lateral size or mean width) and \( t \) thickness. Underlying relations between percolation threshold and aspect ratio was given by Garboczi et al. in their pioneering work (20). They discussed the percolation mechanism of oblate/prolate ellipsoids using excluded volume theory and found that the sphere has the maximum threshold among all the geometries while at the limit of thin sheets (e.g., graphene) threshold is linearly proportional to the \( 1/\alpha \). Excluded volume which is the spatial region prohibiting coexistence of the centers of two topologically similar particles has been used for a long time to study percolation behavior (31). In one of the most important example of this model, percolation threshold of disk-like particles was estimated using excluded volume as an interval (32):

\[ 1 - \exp\left(-\frac{3.6}{\pi \frac{1}{\alpha}}\right) \leq \phi_c \leq 1 - \exp\left(-\frac{5.6}{\pi \frac{1}{\alpha}}\right) \]  

(2)

Excluded volume theory is a quite successful and accepted approach but most of the time needs a numerical evaluation and its exact definition is a topologically stiff problem (20,33). Monte Carlo simulation is also frequently preferred to solve the percolation mechanism (34). The first prediction of percolation threshold of 3D randomly oriented objects was carried out by Balberg et al. using Monte Carlo (35). Balberg also utilized
this simulation method in the analysis of excluded volumes and obtained universal values for different geometries (36). Monte Carlo simulation predicted the threshold value of isotropically oriented disks as an inverse scaling \( \phi_c \approx 1.46 \frac{1}{\alpha} \) for \( \alpha \gg 1 \) (37). Recently, Baniassadi et al. added electron tunneling distance into the Monte Carlo simulation of GNP percolation but the predictions are considerably lower than the experimental data (38). Numerical works and simulations have yielded amazing results last three decades, but they are system-specific and in practice highly time-consuming (39). However in material design, analytical laws which are easy in assessment and manipulation are expected. In order to develop a model satisfying these criteria, we will focus on inverse aspect ratio scaling of percolation threshold of nonspherical particles which is now a well-known fact in literature (20,34,37,40,41). Celzard et al. (32) applying excluded volumes to graphite and carbon fiber based polymer composites achieved the relation of:

\[
\phi_c \propto \frac{t}{D} = \frac{1}{\alpha}
\]

which is applicable in whole range of aspect ratio, from disks to rods. Li and Kim formulated the percolation threshold of GNPs as a function of geometry and distribution in polymer matrix (42):

\[
\phi_{c,2D}^{2D} = \frac{2\pi D^2 t}{(D + \zeta)^3}, \quad \phi_{c,3D}^{3D} = \frac{27\pi D^2 t}{4(D + \zeta)^3}
\]

where, \( \phi_{c,2D}^{2D} \) and \( \phi_{c,3D}^{3D} \) are the percolation thresholds for 2D plane and 3D spatially random particle distribution in composites, and \( \zeta \) is the inter-particle distance between GNPs, respectively. 3D isotropic distribution is the common situation; however in oriented systems, layer-by-layer coatings, graphene papers etc., GNPs could have a planar positional correlation. Despite its capabilities, in evaluation of equation (4) one simultaneously needs to know \( D, t \) along with \( \zeta \) being very hard to measure. In order to solve this closed form, we will take \( D \gg \zeta \) which is a reasonable assumption in vicinity of the threshold. After simple algebraic manipulation and this assumption, Equation (4) will reduce to the following forms, a modified version of inverse proportionality:

\[
\phi_{c,2D}^{2D} = 2\pi \frac{1}{\alpha}, \quad \phi_{c,3D}^{3D} = \frac{27\pi}{4} \frac{1}{\alpha}
\]

The effect of aspect ratio on the threshold can be explained by network or graph analogy with complex percolation clusters of the particles. If we map our distributed particle system onto a graph \( G(E, V) \) in which the conducting objects are vertices and tunneling currents between them are edges, then composite structure of the dispersed particles in polymer would form a tunneling interaction network (See Figure 1c) (30,43). If the probability of edge formation between vertices are uniformly equal to \( p \in (0,1) \) and independent from each other, this tunneling interaction network is known as random or Erdös-Renyi graph and has a percolation threshold at (21):

\[
\phi_c = \frac{1}{\langle k \rangle}
\]

where \( \langle k \rangle \) is the network degree, i.e. mean number of connections between vertices. Chatterjee also used a similar analogy to model percolation of rod-like particles with
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length of L and radii of R as a Bethe lattice network and found \( \phi_c = 1/(k - 1) \approx R/L \) for monodisperse rods (44). However, unlike these simplified models, vertices of real networks connect preferentially leading to crowded and dense “cliques” or “flocks” in the network. This makes clustering effects dominant at which the threshold should be predicted with a tuning parameter of cluster fraction (45). Meaning of above topological concepts can be easily re-linked to the parameters of actual nanocomposite. In a percolation cluster, electron tunneling can be occurred only between the particles which are closest being enough to cross the potential barrier. Hence, k degree of tunneling interaction network will be the number of the nearest neighbors of particles. Such a concept is well known in the theory of granular media employing similar contact network analogies for correlations of particles in a packing. In this definition, degree of contact network is the coordination number, \( \langle z \rangle \) which is the mean number of closely packed particles around each particle (46). In the case of non-spherical particles, a direct relation \( \langle z \rangle \sim \alpha \equiv D/t \) is appeared in numerous studies (47–50). \( \langle z \rangle \) has a minimum for spheres and increases continuously for increasing shape anisotropy of rods and disks (51). Clearly, correspondence principles between percolation clusters, networks and granular systems will allow one to write \( \langle z \rangle \sim D/t \) into the percolation threshold of Erdös-Renyi networks (equation (6)):

\[
\phi_c = \frac{1}{\langle z \rangle} \propto \frac{1}{\alpha}
\]  

which is the same result of well-known inverse proportionality Eq. 3. We could derive and prove this general relation using only simple geometrical concepts but, like other counterparts from literature, still it is not valid for the real nanocomposites in which the nanostructured components have a strong tendency to aggregation. Particle agglomeration and phase separation in polymer nanocomposites due to the entropic forces emanating from weak interaction energy at polymer-nanoparticle interface is a common process (52,53). Therefore, we speculated a phenomenological relation considering clustering effects qualitatively:

\[
\phi_c = \kappa \frac{1}{\alpha}
\]  

where \( \kappa \) is a factor defining the extent of clustering and departure from completely random network formation, that is, increasing \( \kappa \) is the signature of stronger agglomeration of the particles in polymer matrix. Equation (8) was studied to evaluate its applicability and determine the range of \( \kappa \) using literature collected data (4,5,7–10,13–15,22,24,25,27,28,54–61). Unfortunately, finding meaningful experimental data, such as the exact size of GNPs, in literature was a tough problem. Hence we carefully confirmed data by both text and microscopy images of the papers, and discarded all the unclear works without any bias. Figure 2 shows pretty well fitting of literature data with our approach, (equation (8)). With the help of its simple nature, equation (8) was highly efficient in usage; from GNPs to mono-/few-layer graphene, percolation threshold could be predicted just by assigning an appropriate \( \kappa \) value. Smaller \( \kappa \leq 1 \) was especially suitable in describing mono-/few-layer graphene and GNPs. Note that excluded volume theory (equation (2)), modified Li-Kim model (equation (5)) and previous numerical studies (20, 37) found similar trends for their thresholds. But treating this relationship as a phenomenological equation with arbitrary \( \kappa \) would evidently lead to more versatile formulation. For example, GNP-high density polyethylene (HDPE) (60) and thermally
Figure 2. Comparison of theoretical percolation threshold predicted by equation (8) (solid lines) and literature data (circles). Data points correspond to the nanocomposites of single-/few-layer (above) and multi-layer graphene, i.e. GNPs (bottom) hosted in the entitled polymer. $\kappa = 1, 2, 3, 4, 5$ and $20$. Green region is the representative area of threshold interval of excluded volume theory, (equation (2)). Dashed curves $\phi_c^{2D}$ and $\phi_c^{3D}$ are the modified Li-Kim model (equation (5)) (color figure available online).

reduced graphite oxide-polyamide 6 (RO-PA6) (10) composites presented higher $\kappa$ up to $\gg 20$ (See Figure 2) that can not be described by conventional methods except $\phi_c^{3D}$ of equation (5). But still $\phi_c^{3D}$ defined area is far from the region of real graphene systems. Another interesting point was the effect of polymer matrix. As mentioned before, chemistry of macromolecular environment controls the dispersibility of GNPs and determine nanostructure of the clusters where electrons are transported. $\phi_c$ of RO- series composites of (10) in Figure 2 showing different $\phi_c$ for different polymers could be ascribed to this effect. Fabrication method is also an important factor, namely solution based methods tend to offer smaller $\phi_c$ contrary to melt compounding probably due to the diffusion limitations in viscous melt. However we left detailed discussion of $\kappa$ in the light of macro-molecular structure of the matrix and spatial distribution of GNPs as a future problem. In addition to graphene nanostructures, our model was also applied to bulk carbon materials such as graphite, carbon black and expanded graphite (see Supporting Information, Figure S1). As expected, low aspect ratio of them resulted in somewhat lower model consistency.
2.2. Critical Exponent

Critical exponent problem has attracted great attention for many years in different fields as a phase transition concept (18,62–66). Unfortunately available studies have been limited to the constant/universal values of the exponent and complex real systems have not been investigated in depth. Balberg et al. (67) attempted to model the critical exponent of carbon black-polymer composites as a function of particle diameter and distribution. However their model could not agree with the experimental data and was not applicable for non-spherical particles. Stephen used mean-field and renormalization-group approaches for random resistor networks based on an analogy with conduction in heterogeneous materials and suggested that system dimensionality dictates the exponent as $s_d = 3 - \frac{11}{42}(6 - d)$; $d: 1, 2, 3$ (68,69). In cases in which the nonuniversal critical exponent was relevant, Shao et al. achieved equation (9) being able to calculate wide range of $s$ (70): \[
s = s_{un} + \varepsilon \left( \frac{p_D}{p_B} \right) - 1 \tag{9}\]

where $s_{un}$ is the universal critical exponent, $\varepsilon$ is a structure factor, $p_D$ and $p_B$ are number fractions of dangling ends and backbone framework, respectively. Backbone framework is the subgroup of infinite percolation cluster and responsible for the transport of all the current while dangling ends are the remaining part, that is, branched dead-ends playing no role in current conduction (30). Interestingly, there is no powerful method in literature to predict $\langle p_D/p_B \rangle$ ratio from simple parameters. However it is known that backbone fraction is a function of particle aspect ratio (44). Critical exponent of carbon nanotubes also was shown to decrease with increase in their aspect ratio (71). Thanks to this trend which is quite similar to aspect ratio dependence of the percolation threshold, we will try to obtain a self-consistent final formulation for percolation law which is only function of GNP geometry. Under this inverse problem, we heuristically supposed $\langle p_D/p_B \rangle$ as the ratio of lateral surface (dangling ends) to planar surface (backbone) area of GNPs: \[
\left\langle \frac{p_D}{p_B} \right\rangle \equiv \frac{\pi D_t}{\pi D^2} = 2 \frac{1}{\alpha}\]

If we combine this result with Stephen’s universal exponent (as $s_{un} = s_d$) in equation (9), we will have a general equation for critical exponent as a function of system dimensionality and particle geometry: \[
s = 2 - \frac{11}{42}(6 - d) + 2\varepsilon \frac{1}{\alpha} \tag{10}\]

Surprisingly, we found a close agreement (see Figure 3) between equation (10) and literature data (5,7,14,22–24,26–28,59). Both universal and nonuniversal exponents e.g. $s = 5$ could be predicted efficiently and general trend of aspect ratio dependence was well fitted. Interestingly, graphene, GNPs and expanded graphite could have same $\varepsilon$ value pointing out that they can build topologically similar mesoclusters during percolation. Additionally, there was no apparent relation between nanoparticle structure and critical exponent. For example, exponents of expanded graphite-phenolic resin and graphene-UHMWPE composites were in the same range of $s \approx 1.5$. To the best of our knowledge, equation (10) is one of the first implementation of the critical exponent in terms of well-known topological GNP properties. Finally, correlation possibility between clustering factor $\kappa$ and cluster
Figure 3. Comparison of theoretical critical exponent predicted by Eq. 10 (solid lines) which is plotted for 3D \( (d=3) \) random distributed particles and literature data (circles). \( s^{2D} \) and \( s^{3D} \) are the generally accepted universal exponents for \( d=2 \) and \( d=3 \) dimensional particle distribution. Titles of circles correspond to components of the nanocomposite systems. For other acronyms please see the legend of Figure 2 (color figure available online).

2.3. Effective Conductivity and Temperature Dependence

The last term to be discussed is the effective conductivity \( \sigma_e \) which has been incorrectly considered as the conductivity of graphite nanofiller. However, \( \sigma_e \) is in the range of \( 1-10^3 \) S/cm (7, 8, 28) in comparison to \( \sigma_{\text{Graphene}} = 10^6 \) S/cm. This discrepancy can be interpreted by low conductivity of GNP-polymer interphase limiting the ultimate quality with \( \sigma_e/\sigma_{\text{Graphene}} \ll 1 \). Moreover, evaluating \( \sigma_e \) as a constant leads to the difficulty of temperature independent nanocomposite conductivity. In order to overcome these issues, charge transport mechanisms of GNPs should be elaborated. Resistivity of graphene-metal contact was measured at the level of \( 10^2-10^3 \) \( \Omega \cdot \mu m^2 \) (72,73) and probably it will be larger for the interfaces to an insulator. Phonon scattering is the main reason of the electrical resistance in GNP nanostructures surrounded by an insulator (74):

\[
R_{\text{GNP}}(V_g, T) = R_0(V_g) + R_A(T) + R_{B-E}(V_g, T) \tag{11}
\]

where \( R_0(V_g) \) is the residual resistance at low temperature, \( R_A(T) \) is the resistance due to the acoustic phonon scattering in graphene and \( R_{B-E}(V_g, T) \) is the resistance arising at the graphene-insulator interphase via remote phonon scattering obeying Bose-Einstein statistics (74):

\[
R_A(T) = \left( \frac{h}{e^2} \right) \frac{\pi^2 D_k^2 k_B T}{2h^2 \rho A v_F^2} \quad \text{and} \quad R_{B-E}(V_g, T) = B V_g^{1/a} \left( e^{\frac{E_g}{k_B T}} - 1 \right)^{-1}
\]

where \( V_g \) is the gate (measurement) voltage, \( T \) is the absolute temperature, \( e = 1.60 \times 10^{-19} C \) is the elementary charge, \( h = 6.63 \times 10^{-34} \) J\( s \) is the Planck’s constant, \( k_B = \)
1.38 × 10^{-23} JK^{-1} is the Boltzmann constant, \( \rho_t = 7.6 \times 10^{-7} \text{ kgm}^{-2} \) is the planar density of graphene, \( v_F = 1 \times 10^6 \text{ ms}^{-1} \) is the Fermi velocity, \( v_s = 2.1 \times 10^4 \text{ ms}^{-1} \) is the velocity of sound for acoustic phonons, \( D_A = 2.88 \times 10^{-18} \text{ J} \) is the acoustic phonon deformation potential, \( B = 3.26(h/e^2) \), \( a = 1.02 \) and \( E_0 = 1.67 \times 10^{-20} \text{ J} \). \( R_0(V_g) \) can be neglected for elevated temperatures. Equation (11) was derived for graphene-on-SiO\(_2\) nanostructures however it can be used for graphene-PMMA hybrids owing to similar dielectric properties of SiO\(_2\) and PMMA (74). Equation (11) was plotted in Figure 4 for different voltages. Surprisingly, near and above room temperature, and moderate gate voltages, \( \sigma_{GNP}(V_g, T) \) is in the region of 10\(^3\) S/cm. Almost same levels of \( \sigma_{GNP}(V_g, T) \) and \( \sigma_e \) allowed us to write it down as \( \sigma_e = \sigma_{GNP}(V_g, T) \). As a comparison attempt, two different temperature dependent conductivity model was adapted from carbon nanotube literature: variable-range hopping and thermal fluctuation induced tunneling (75). Variable-range hopping gives temperature effect in the form of \( \sigma = \sigma_0(-T_0/T)^{1/4} \) where \( T_0 \) is the hopping temperature. Fluctuation induced tunneling, however, focuses on thermally vanishing tunneling barrier; \( \sigma = \sigma_0(-T_1/(T_0 + T)) \) where \( T_0 \) and \( T_1 \) are the coefficients related to tunneling activation energy. When these models roughly simulated in Figure 4, we observed our approach was more sensitive to temperature. Additionally, their trends have slightly opposite direction, i.e. temperature increase causes negative slope in tunneling model in contrast to the positive change of hopping model. Such unexpected behavior will be rediscussed in section 4.2.

We have discussed and reformulated parameters of the conventional power law. We can now modify the power law through incorporation of filler aspect ratio, spatial distribution in polymer media, dimensionality and temperature dependent conductivity. Rearrangement of equation (1) by writing equations (8, 10, 11) will bring us to the main result of this paper:

\[
\sigma = \sigma_{GNP}(V_g, T) \left( \phi - \frac{\kappa - \alpha}{\alpha} \right)^{2-\frac{11}{2}/(6-\delta)+2\epsilon} \frac{1}{2}
\]

(12)

**Figure 4.** Electrical conductivity of GNPs embedded in an insulating media as a function of temperature and gate voltage. Conductivity–temperature correlation becomes stronger as the voltage decreases. Variable-range hopping (VRH) and fluctuation induced tunneling (FIT) trend lines were simulated simply assuming \( T_0 = T_1 = 200 \text{ K} \) (color figure available online).
As a semi-analytical relationship, equation (12) is suitable for simple engineering design calculations. Each variable is well known and choosing only phenomenological factors is sufficient to solve it. In similar studies one could use numerous other percolation models from literature but for convenience we preferred generally accepted power law and exactly defined parameters. Moreover, equation (12) will also be highly useful for other hybrid materials containing plate-like nanostructures. It should be noted here that equation (12) will be applicable only up to first next phase transition temperature of the polymer e.g. softening point. This is a serious issue frequently ignored by the researchers. At higher temperature, macromolecular vibrations could change the microstructure and interactions, which will need redefinition of related parameters.

3. Experimental Methods

Pristine GNPs were produced from ionic graphite intercalation compounds (GICs) in bulk scale by Hayzen Engineering Co. using proprietary process intensification approaches. In comparison to traditional graphene oxide containing large number of surface groups such as hyroxyl and epoxy as a crystal defect, we could synthesize GNPs without heavy oxidation as proved by XPS C1s and O1s spectra showing 90% elemental carbon composition (see Supporting Information, Figure S3). GNPs were surface functionalized by vinyl acetate or butyl acrylate through a method similar to (76,77). Briefly, 0.5wt% aqueous sodium dodecyl sulfate (SDS) solution, 1 mg/mL (per volume of water-SDS solution) pristine GNPs and 0.0625 % v/v (per volume of water-SDS solution) vinyl acetate or butyl acrylate monomer were mixed and sonicated for 30 min. Suspensions were chilled to 6°C for one week and then precipitated in excess volume of methanol. Final products were filtered and dried in 50°C oven for 24 hours. The samples of pristine GNPs, vinyl acetate-and butyl acrylate-functionalized GNPs were designated as P-GNPs, V-GNPs and B-GNPs, respectively. Natural graphite (−325 mesh) was used as macro-particle comparison. The nanocomposite samples were fabricated using two (solid and liquid) component PMMA resin system (Hayzen Engineering Co.) ensuring low shrinkage polymerization. The solid component is composed of PMMA powder (0.90 – 1.50 × 10^6 g/mol, average particle size 32–48 μm) and benzoyl peroxide while the liquid component is the methyl methacrylate (MMA) monomer with other additives. Preparation of the nanocomposite sample started by dispersing GNPs in liquid component by 30 min ultrasonication yielding quite homogeneous suspensions since MMA is a highly polar solvent. The dispersion was then blended by solid component (solid/liquid: 50/50 w/w) until a grayish uniform viscous gel was obtained and finally the gel was casted on glass substrates via 50°C curing for 20 minutes.

Nanostructure of GNPs was determined by transmission electron microscopy (TEM) imaging using Jeol JEM1010 with MegaViewIII CCD camera (Soft Imaging System–Olympus now) and 80 kV accelerating voltage. For thickness measurements of GNPs, six TEM images were taken randomly at different magnification and the thickness was measured at five distinct location (but same for each images). These measurements were used to plot the thickness histograms reported in following chapters. TEM specimens of the nanocomposites were also cut from bulk blocks as 70 nm thin sections using a Leica UC6 ultramicrotome (diamond knife, Diatome) via Epon epoxy embedding and then analyzed directly. Scanning electron microscopy (SEM, FEI Quanta 3D FEG, 30kV accelerating voltage) was used to observe the morphology of GNPs and GNP/PMMA nanocomposites at their fractured surfaces. We probed structural parameters of the pristine GNPs and their nanocomposites by Raman spectroscopy in 6–3500 cm\(^{-1}\) range using Bruker Dispersive Raman spectrometer with 532 nm Nd-YAG laser as well as X-ray
diffraction (XRD, Rigaku Ultima-IV, Cu/40 kV/30 mA). Elemental composition of GNPs was characterized using X-ray photoelectron spectroscopy (XPS) using an SPECS EA-200 instrument and Al Kα radiation (energy 1486.6 eV). Electrical volume resistivity was measured by two-probe method employing embedded copper electrodes eliminating contact resistance (78).

4. Results and Discussion

4.1. Structural Characterization

Topology and structural quality of the GNPs were revealed by TEM investigation in Figure 5. Unlike conventional graphite oxide based graphene which has highly crumpled layers, synthesized GNPs are free from defects. Polymer functionalization in V-GNPs and B-GNPs was proved as nanoparticles decorating GNP surfaces that can be seen in Figure 5bI and Figure 5cII as indicated by arrows. Highly crystalline graphene layers inhibited the random disruption/etching of atomic edges and resulted in straight parallel lines shown in Figure 5bII. Thicknesses of three types of GNPs were assessed by the histograms at column III of Figure 5. Student’s t test (unpaired, two-tailed, \( p < 0.05 \)) showed that there was no statistically significant difference in the thickness means of GNP types. General average of thickness was \( \sim 15 \) nm corresponding to \( \sim 44 \) layers (single layer Van der Waals thickness of graphene is 0.34 nm (1)). We also looked for the diameter of GNPs and bulk

![Figure 5](image)

**Figure 5.** TEM images of P-GNPs (a), V-GNPs (b) and B-GNPs (c); corresponding thickness histograms with the solid lines as best fits are plotted at right, respectively. In main text, each row are enumerated from left to right by increasing Roman numbers (color figure available online).
graphite powder using SEM images (see Supporting Information, Figure S4–S7). Along with some large area platelets, the diameter of GNPs was approximately in the range of 5–10 μm while graphite powder was in the form of irregular μm-scale particles.

Figure 6 illustrates typical nanostructure of the PMMA nanocomposites based on SEM and TEM imaging. The arrows in the SEM images point to the pulled-out GNPs on fractured PMMA surfaces. In Figure 6bI one can see the previously mentioned densely agglomerated GNP morphology defined by κ as irregularities in contrast to the smooth areas of bare polymer matrix. Such a morphology should be related to insufficient solubility of some PMMA particles from the solid component. During the polymerization of GNP/MMA suspension, GNPs should be confined in the spaces between undissolved PMMA particles. Nevertheless, Figure 6aI and cI still suggest that the composition was quite uniform. We also reported TEM characterization from cross-section of the nanocomposites. Figure 6aII was given intentionally as a good representation of the hypothetical charge carrier conduction path, i.e. infinite percolation cluster. In addition to coarsely crumpled P-GNPs in Figure 6aIII, successfully exfoliated P-GNPs consisting only a few graphene layers were also observed at inset. V-GNPs offered us a highly interesting nanostructure in Figure 6bIII. We highlighted border of this V-GNP oriented in same direction of ultramicrotome slicing. Large arrow indicates a folded point like a sheet of paper referring superior flexibility of graphene. TEM images of B-GNP based composites had also unique morphologies. Especially in Figure 6cIII, elongated graphene nanoribbon structures can be seen.
The extent of exfoliation and interaction of GNPs with PMMA can be evaluated by Raman spectroscopy and XRD. In Figure 7, Raman spectra which is an excellent tool to structurally characterize carbon materials showed exceptional crystalline perfection of our GNPs deduced from almost invisible D band (near 1350 cm$^{-1}$). The ratio of 2D band (near 2700 cm$^{-1}$) to G band (near 1580 cm$^{-1}$) is gradually diminished with increased number of graphene layers (1,79). In our case, $I_{2D}/I_G$ was increased approximately 50% referring to partial exfoliation of GNPs in PMMA. In Figure 8, XRD pattern of P-GNPs shows an apparent 26.5° diffraction peak for (002) planes contrary to graphite oxide with $2\theta_{(002)}$ below 20° as well as graphene with no visible peak at XRD pattern (16). Since our ionic GIC based process yields multilayer graphene, it is natural to observe the diffraction peak for (002) planes. However this low cost process is remarkably effective yet as evidenced by Raman spectra and other characterization data. Recently Shih et al. (79) proposed a novel synthesis approach quite similar to ours giving excellent quality bi-/tri-layer graphene. In there, serious problems related to graphite oxide and their defective graphene products were discussed at length. They also observed similar XRD patterns even after thermal expansion. Additionally, XRD characterization was utilized for PMMA nanocomposites containing 0.5 vol.% P-GNPs. Minor 26.5° peak in GNP-polymer nanocomposites are widely appeared in literature like (9). Unfortunately we could not acquire XRD pattern of V-GNP and B-GNP which may be exfoliated in PMMA matrix more efficiently.

4.2. Model Validation with Experimental Electrical Data

Electrical conductivity of the nanocomposites synthesized in this study can now be discussed using the models developed in previous sections. DC conductivity measurements were performed for the samples with increasing GNP content. Unfortunately,
our measurement setup limited us to study conductivity only higher than $10^{-10}$ S/cm. Therefore, we assigned conductivity of PMMA as data points below $10^{-10}$ S/cm causing the absent data in this region up to percolation. For the evaluation of the percolation behavior, we first fitted the measured electrical conductivities by equation (12) in constant temperature regime. In order to attain the best fitted curve, $\phi_c$ was detected experimentally as the first GNP content where the conductivity was higher than $10^{-9}$ S/cm. $\kappa$ was calculated using this experimental $\phi_c$ and assuming $D/t = 7.5 \, \mu m/15 \, nm$ as shown by TEM and SEM analysis. Then equation (12) was simulated for $\sigma_e = 10^3$ S/cm, $d = 3$, $D/t=500$ and varying $\varepsilon$ until the closest fitted curve was plotted. Once the curve was obtained, we recorded all the parameters used to fit. This way of calculation instead of traditional logarithmic evaluation of the power law was intentionally chosen to see capabilities of our modified model. Confirming that, equation (12) precisely fitted the percolation trend of our composite samples (See Figure 9).

Fitting accuracy was the highest for P-GNP and V-GNP based PMMA nanocomposites and followed by B-GNP. We also tabulated the fitting parameters of equation (12) for each curve. The assumption of $\sigma_e = 10^3$ S/cm in the calculation above was found to be admissible supporting our claims on phonon scattering controlled resistivity given by
Figure 9. Electrical conductivity of GNP filled PMMA nanocomposites as a function of volume fraction. The solid lines are the best fits to equation (12). Calculated parameters of equation (12) are listed for each curve.

equation (11). Calculated $\kappa$, $\varepsilon$ and $s$ were all in the range of the literature data in Figures 2 and 3. Higher values of $\varepsilon$ can be described related to our PMMA system. Solid/liquid mixed composition distorted topology of infinite percolation cluster (mesoclusters) of GNPs in some cases such as Figure 6b1 that is the reason of higher $\varepsilon$. Different $\kappa$ of each GNP type was only due to the surface chemistry related miscibility leading variation in agglomeration density. Geometrical effect of thin soft coatings on percolation of disks like our polymer coated GNPs was studied by Ambrosetti et al. and they found that the effect vanishes at $\alpha \to \infty$ limit (39). $\varepsilon$ was not affected at the same level as can be seen in Figure 3. Similar to literature, different nanostructures may build similar clusters at mesoscale and clearly $\varepsilon$ was defined as mesocluster structure factor in equation (10). However, phenomenological factors $\kappa$ and $\varepsilon$ need more emphasis on their meaning in view of future studies. Note that, percolation thresholds of B-GNP/PMMA composites, 0.3 vol.% is lower than $\sim$90% of the literature available to us (see Figure 2 and related text) and our maximum achievable conductivity, $\sim 10^{-1}$ S/cm is at the upper level among other studies indicating high quality of the nanocomposites. In comparison to GNPs, micro-graphite particles ($\sim 325$ mesh) exhibited distinctive percolation behavior. We could not fit the electrical conductivity of micro-graphite using $\sigma_e = 1000$ S/cm assumption and we had to re-evaluate equation (12) for $\sigma_e = 1$, 100 and 1000 S/cm using same procedure. Thus, we found that similar to other low aspect ratio fillers such as carbon black, expanded graphite etc., our graphite powder
Figure 10. Electrical conductivity of 0.5 vol.% GNP filled PMMA nanocomposites as a function of temperature. Recorded conductivity is normalized to the value at 303 K, i.e. $\sigma_0$. The solid line is the normalized equation (12) as $\frac{\sigma_{\text{GNP}}(V_g, T)}{\sigma_{\text{GNP}}(V_g, 303)}$.

showed higher critical exponent and very small $\varepsilon$. Finally, “nano-enhancement effect” of GNPs in percolation threshold up to 50-fold in comparison to ordinary graphite should be underlined.

The effect of temperature on the electrical conductivity of the samples was monitored and modeled for 0.5vol% GNP containing PMMA nanocomposites (see Figure 10). Temperature dependent data and equation (12) were normalized to the conductivity value at 303 K to display them more visually. It was observed that the agreement between data and equation (12) was notably fine at elevated temperatures. However, at low temperatures around 250–300 K, experimental data significantly deviated from equation (12). Unusual temperature dependence of electrical conductivity is a well known phenomenon in carbon material filled polymers whose resistivity can both increase and decrease with temperature (9,80–82). Fan et al. studied conductivity of Al$_2$O$_3$-graphene system from 2 to 300 K (27) and measured a linearly increasing conductivity in contrast to our raw data. They attributed this behavior to semimetallic electron transport. Similar findings in the range of 50–420 K were explained by tunneling based conductivity (83). Zheng et al. argued that the rheological evolution of GNPs in polymer matrix due to the heating/cooling results in the temperature dependence anomaly (80). Above scheme proved our claims on the validity of temperature-conductivity correlation being range specific. Storage modulus of PMMA experiences a drop at 40–60°C while below room temperature modulus increases denoting macromolecular locking (84). Restricted mobility of GNPs will give smaller slope in temperature-conductivity curve. We should note that, improvement of our model to obtain better predictions in temperature dependent conductivity will be evaluated as a future research direction.

5. Conclusions

We developed a simply modified power law model for the percolation theory of electrically conductive graphene-based polymer nanocomposites. The model was discussed in view of graphene geometry, volume fraction at the threshold and critical exponent of the power law collected from the existing literature data. In Figures 2 and 3, it was revealed that our
formulation agreed with the percolation parameters of the literature. The authors hope that the information summarized in these figures could serve as a reference for the researchers who study in related fields. We also prepared pristine and surface functionalized GNP to be used for in situ polymerized PMMA nanocomposites. Electrical conductivity of the fabricated nanocomposites were predicted with high accuracy at both constant and varying temperature regimes. Possible discrepancies between the modified power law and our percolation data were examined. Proposed simple and efficient model can be utilized in the engineering of technologically important conductive graphene-polymer hybrids.

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Supplemental Material

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References

1. Singh, V., Joung, D., Zhai, L., Das S., Khondaker S. I., and Seal S. (2011) Graphene based materials: Past, present and future. *Prog. Mater. Sci.*, 56: 1178–1271.
2. Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Katsnelson, M. I., Grigorieva, I. V., Dubonos, S. V., and Firsov, A. A. (2005) Two-dimensional gas of massless Dirac fermions in graphene. *Nature*, 438: 197–200.
3. Pan, Y.-X., Yu, Z.-Z., Ou, Y.-C., and Hu, G.-H. (2000) A new process of fabricating electrically conducting nylon 6/graphite nanocomposites via intercalation polymerization. *J. Polym. Sci. Part B*, 38: 1626–1633.
4. Chen, G.-H., Wu, D.-J., Weng, W.-G., and Yan, W.-L. (2001) Dispersion of graphite nanosheets in a polymer matrix and the conducting property of the nanocomposites. *Polymer Eng. Sci.*, 41: 2148–2154.
5. Chen, G., Weng, W., Wu, D., and Wu, C. (2003) PMMA/graphite nanosheets composite and its conducting properties. *Eur. Polym. J.*, 39: 2329–2335.
6. Shen, J.-W., Chen, X.-M., and Huang, W.-Y. (2003) Structure and electrical properties of grafted polypropylene/graphite nanocomposites prepared by solution intercalation. *J. Appl. Polym. Sci.*, 88: 1864–1869.
7. Weng, W., Chen, G., Wu, D., Chen, X., Lu, J., and Wang, P. (2004) Fabrication and characterization of nylon 6/foliated graphite electrically conducting nanocomposite. *J. Polym. Sci. Part B*, 42: 2844–2856.
8. Stankovich, S., Dikin, D. A., Dommett, G. H. B., Kohlhaas, K. M., Zimney, E. J., Stach, E. A., Piner, R. D., Nguyen, S. T., and Ruoff, R. S. (2006) Graphene-based composite materials. *Nature*, 442: 282–286.
9. Ansari, S. and Giannelis, E. P. (2009) Functionalized graphene sheet-poly(vinylidene fluoride) conductive nanocomposites. *J. Polym. Sci. Part B*, 47: 888–897.
10. Steurer, P., Wissert, R., Thomann, R., and Mulhaupt, R. (2009) Functionalized graphenes and thermoplastic nanocomposites based upon expanded graphite oxide. *Macromol. Rapid Commun.*, 30: 316–327.
11. Yoonessi, M. and Gaier, J. R. (2010) Highly conductive multifunctional graphene polycarbonate nanocomposites. *ACS Nano*, 4: 7211–7220.
12. Ning, D., Chao-yue, Z., Qiao, C., Gang, W., and Rong, L. (2010) Preparation and characterization of nylon 6/graphite composite. Mater. Chem. Phys., 120: 167–171.
13. Lee, H. B., Raghu, A. V., Yoon, K. S., and Jeong, H. M. (2010) Preparation and characterization of poly(ethylene oxide)/graphene nanocomposites from an aqueous medium. J. Macromol. Sci. B, 49: 802–809.
14. Zhang, H.-B., Zheng, W.-G., Yan, Q., Yang, Y., Wang, J.-W., Lu, Z.-H., Ji, G.-Y., and Yu, Z.-Z. (2010) Electrically conductive polyethylene terephthalate/graphene nanocomposites prepared by melt compounding. Polymer, 51: 1191–1196.
15. Vadukumpully, S., Paul, J., Mahanta, N., and Valiyaveetil, S. (2011) Flexible conductive graphene/poly(vinyl chloride) composite thin films with high mechanical strength and thermal stability. Carbon, 49: 198–205.
16. Zhou, T., Chen, F., Tang, C., Bai, H., Zhang, Q., Deng, H., and Fu, Q. (2011) The preparation of high performance and conductive poly (vinyl alcohol)/graphene nanocomposite via reducing graphite oxide with sodium hydrosulfite. Compos. Sci. Technol., 71: 1266–1270.
17. Kirkpatrick, S. (1973) Percolation and conduction. Rev. Mod. Phys., 45: 574–588.
18. Balberg, I. (1987) Tunneling and nonuniversal conductivity in composite materials. Phys. Rev. Lett., 59: 1305–1308.
19. Nan, C.-W., Shen, Y., and Ma, J. (2010) Physical properties of composites near percolation. Annu. Rev. Mater. Res., 40: 131–51.
20. Garboczi, E. J., Snyder, K. A., Douglas, J. F., and Thorpe, M. F. (1995) Geometrical percolation threshold of overlapping ellipsoids. Phys. Rev. E, 52: 819–828.
21. Li, G., Braunstein, L. A., Buldyrev, S. V., Havlin, S., and Stanley, H. E. (2007) Transport and percolation theory in weighted networks. Phys. Rev. E, 75: 045103.
22. Zhou, L., Lin, J., and Chen, G. (2009) Electrical breakdown in high-density polyethylene/graphite nanosheets conductive composites. J. Polym. Sci. Part B, 47: 576–582.
23. Zhang, X., Shen, L., Xia, X., Wang, H., and Du, Q. (2008) Study on the interface of phenolic resin/expanded graphite composites prepared via in situ polymerization. Mater. Chem. Phys., 111: 368–374.
24. Pang, H., Chen, T., Zhang, G., Zeng, B., and Li, Z.-M. (2010) An electrically conducting polymer/graphene composite with a very low percolation threshold. Mater. Lett., 64: 2226–2229.
25. Li, J., Sham, M. L., Kim, J.-K., and Marom, G. (2007) Morphology and properties of UV/ozone treated graphite nanoplatelet/epoxy nanocomposites. Compos. Sci. Technol., 67: 296–305.
26. Shen, J.-W., Huang, W.-Y., Zuo, S.-W., and Hou, J. (2005) Polyethylene/grafted polyethylene/graphite nanocomposites: Preparation, structure, and electrical properties. J. Appl. Polym. Sci., 97: 51–59.
27. Fan, Y., Wang, L., Li, J., Li, J., Sun, S., Chen, F., Chen, L., and Jiang, W. (2010) Preparation and electrical properties of graphene nanosheet/Al2O3 composites. Carbon, 48: 1743–1749.
28. Srivastava, N. K. and Mehra, R. M. (2008) Study of structural, electrical, and dielectric properties of polystyrene/foliated graphite nanocomposite developed via in situ polymerization. J. Appl. Polym. Sci., 109: 3991–3999.
29. McLachlan, D. S. (1988) Measurement and analysis of a model dual-conductivity medium using a generalised effective-medium theory. J. Phys. C: Solid State Phys., 21: 1521–1532.
30. Sen A.K. et al. (Eds.). (2009) Quantum and Semi-classical Percolation and Breakdown in Disordered Solids. Lect. Notes Phys., 762, Springer: Berlin Heidelberg.
31. Balberg, I., Anderson, C. H., Alexander, S., and Wagner, N. (1984) Excluded volume and its relation to the onset of percolation. Phys. Rev. B, 30: 3933–3943.
32. Celzard, A., McRae, E., Deleuze, C., Durfort, M., Furdin, G., and Mareche, J. F. (1996) Critical concentration in percolating systems containing a high-aspect-ratio filler. Phys. Rev. B, 53: 6209–6214.
33. de Dreuzy, J.-R., Davy, P., and Bour, O. (2000) Percolation parameter and percolation-threshold estimates for three-dimensional random ellipses with widely scattered distributions of eccentricity and size. Phys. Rev. E, 62: 5948–5952.
34. Yi, Y. B. and Tawerghi, E. (2009) Geometric percolation thresholds of interpenetrating plates in three-dimensional space. *Phys. Rev. E*, 79: 041134.
35. Balberg, I., Binenbaum, N., and Wagner, N. (1984) Percolation thresholds in the three-dimensional sticks system. *Phys. Rev. Lett.*, 52: 1465–1468.
36. Balberg, I. (1985) “Universal” percolation-threshold limits in the continuum. *Phys. Rev. B*, 31: 4053–4055.
37. Vovchenko, L. and Vovchenko, V. (2011) Simulation of percolation threshold in composites filled with conducting particles of various morphologies. *Mat.-wiss. u.Werkstofftech*, 42: 70–74.
38. Baniassadi, M., Safdari, M., Ghazavizadeh, A., Garimestani, H., Ahzi, S., Gracio, J., and Ruch, D. (2011) Incorporation of electron tunnelling phenomenon into 3D Monte Carlo simulation of electrical percolation in graphite nanoplatelet composites. *J. Phys. D: Appl. Phys.*, 44: 455306.
39. Ambrosetti, G., Johner, N., Grimaldi, C., Danani, A., and Ryser, P. (2008) Incorporation of electron tunnelling phenomenon into 3D Monte Carlo simulation of electrical percolation in graphite nanoplatelet composites. *J. Phys. D: Appl. Phys.*, 44: 455306.
40. Otten, R. H. J. and van der Schoot, P. (2009) Continuum percolation of polydisperse nanofillers. *Phys. Rev. Lett.*, 103: 225704.
41. Saar, M. O. and Manga, M. (2002) Continuum percolation for randomly oriented soft-core prisms. *Phys. Rev. E*, 65: 056131.
42. Li, J. and Kim, J.-K. (2007) Percolation threshold of conducting polymer composites containing 3D randomly distributed graphite nanoplatelets. *Compos. Sci. Technol.*, 67: 2114–2120.
43. Yi, Y.-B. and Sastry, A. M. (2004) Analytical approximation of the percolation threshold for overlapping ellipsoids of revolution. *Proc. R. Soc. Lond. A*, 460: 2353–2380.
44. Chatterjee, A. P. (2010) Connectedness percolation in polydisperse rod systems: A modified Bethe lattice approach. *J. Chem. Phys.*, 132: 224905.
45. Gleeson, J. P. and Melnik, S. (2009) Analytical results for bond percolation and k-core sizes on clustered networks. *Phys. Rev. E*, 80: 046121.
46. Walker, D. M. and Tordesillas, A. (2010) Topological evolution in dense granular materials: A complex networks perspective. *Int. J. Solids Struct.*, 47: 624–639.
47. Mailman, M., Schreck, C. F., O’Hern, C. S., and Chakraborty, B. (2009) Jamming in systems composed of frictionless ellipse-shaped particles. *Phys. Rev. Lett.*, 102: 255501.
48. Torquato, S. and Stillinger, F. H. (2010) Jammed hard-particle packings: From Kepler to Bernal and beyond. *Rev. Mod. Phys.*, 82: 2633–2672.
49. Wouterse, A. (2008) Random packing of colloids and granular matter. PhD Thesis, Universiteit Utrecht.
50. Delaney, G. W. and Cleary, P. W. (2010) The packing properties of superellipsoids. *EPL*, 89: 34002.
51. Blouwolff, J. and Fraden, S. (2006) The coordination number of granular cylinders. *EPL*, 76: 1095–1101.
52. Mackay, M. E., Tuteja, A., Duxbury, P. M., Hawker, C. J., Van Horn, B., Guan, Z. B., Chen, G. H., and Krishnan, R. S. (2006) General strategies for nanoparticle dispersion. *Science*, 311: 1740–3.
53. Hooper, J. B. and Schweizer, K. S. (2006) Theory of phase separation in polymer nanocomposites. *Macromolecules*, 39: 5133–5142.
54. Lu, W., Lin, H., Wu, D., and Chen, G. (2006) Unsaturated polyester resin/graphite nanosheet conducting composites with a low percolation threshold. *Polymer*, 47: 4440–4444.
55. Wei, T., Luo, G., Fan, Z., Zheng, C., Yan, J., Yao, C., Li, W., and Zhang, C. (2009) Preparation of graphene nanosheet/polymer composites using in situ reduction-extractive dispersion. *Carbon*, 47: 2290–2299.
56. Kim, H. and Macoisko, C. W. (2009) Processing-property relationships of polycarbonate/graphene composites. *Polymer*, 50: 3797–3809.
57. Yu, C. and Li, B. (2008) Morphology and properties of conducting polyvinyl alcohol hydrosulfate/graphite nanosheet composites. *J. Compos. Mater.*, 42: 1491–1504.
58. Lu, W., Weng, J., Wu, D., Wu, C. and Chen, G. (2006) Epoxy resin/graphite electrically conductive nanosheet nanocomposite. *Mater. Manuf. Process.*, 21: 167–171.
59. Lin, H., Lu, W., and Chen, G. (2007) Nonlinear DC conduction behavior in epoxy resin/graphite nanosheets composites. *Physica B*, 400: 229–236.

60. Chen, G., Chen, X., Wang, H., and Wu, D. (2007) Dispersion of graphite nanosheets in polymer resins via masterbatch technique. *J. Appl. Polym. Sci.*, 103: 3470–3475.

61. Kalaitzidou, K., Fukushima, H., and Drzal, L. T. (2007) A new compounding method for exfoliated graphite–polypropylene nanocomposites with enhanced flexural properties and lower percolation threshold. *Compos. Sci. Technol.*, 67: 2045–2051.

62. Kogut, P. M. and Straley, J. P. (1979) Distribution-induced non-universality of the percolation conductivity exponents. *J. Phys. C: Solid State Phys.*, 12: 2151.

63. Halperin, B. I., Feng, S., and Sen, P. N. (1985) Differences between lattice and continuum percolation transport exponents. *Phys. Rev. Lett.*, 54: 2391–2394.

64. Golden, K. (1990) Convexity and exponent inequalities for conduction near percolation. *Phys. Rev. Lett.*, 65: 2923–2926.

65. Fisch, R. and Harris, A. B. (1978) Critical behavior of random resistor networks near the percolation threshold. *Phys. Rev. B*, 18: 416–420.

66. Grassberger, P. (1999) Conductivity exponent and backbone dimension in 2-d percolation. *Physica A*, 262: 251–263.

67. Balberg, I., Azulay, D., Toker, D., and Millo, O. (2004) Percolation and tunneling in composite materials. *Int. J. Mod. Phys. B.*, 18: 2091–2121.

68. Stephen, M. J. (1978) Mean-field theory and critical exponents for a random resistor network. *Phys. Rev. B*, 17: 4444–4453.

69. Harris, A. B., Lubensky, T. C., Holcomb, W. K., and Dasgupta, C. (1975) Renormalization-group approach to percolation problems. *Phys. Rev. Lett.*, 35: 327–330.

70. Shao, W. Z., Xie, N., Zhen, L., and Feng, L. C. (2008) Conductivity critical exponents lower than the universal value in continuum percolation systems. *J. Phys.: Condens. Matter*, 20: 395235 (5pp).

71. Foygel, M., Morris, R. D., Anez, D., French, S., and Sobolev, V. L. (2005) Theoretical and computational studies of carbon nanotube composites and suspensions: Electrical and thermal conductivity. *Phys. Rev. B*, 71: 104201.

72. Venugopal, A., Colombo, L., and Vogel, E. M. (2010) Contact resistance in few and multilayer graphene devices. *Appl. Phys. Lett.*, 96: 013512.

73. Nagashio, K., Nishimura, T., Kita, K., and Toriumi, A. (2010) Contact resistivity and current flow path at metal/graphene contact. *Appl. Phys. Lett.*, 97: 143514.

74. Chen, J.-H., Jang, C., Xiao, S., Ishigami, M., and Fuhrer, M. S. (2008) Intrinsic and extrinsic performance limits of graphene devices on SiO2. *Nat. Nanotechnol.*, 3: 206–209.

75. Kymakis, E. and Amaratunga, G. A. J. (2006) Electrical properties of single-wall carbon nanotube-polymer composite films: Electrical and thermal conductivity. *Phys. Rev. B*, 71: 104201.

76. Xia, H., Wang, Q., and Qiu, G. (2003) Polymer-encapsulated carbon nanotubes prepared through ultrasonically initiated in situ emulsion polymerization. *Chem. Mater.*, 15: 3879–3886.

77. Qiu, J., Guo, Z., Xiliang Z., and Chifei W. U. (2006) Preparation of poly (n-butyl acrylates) encapsulated carbon black via ultrasonic irradiation initiating emulsion polymerization. *Polym. J.*, 38: 1245–1250.

78. Han, B., Guan, X., and Ou, J. (2007) Electrode design, measuring method and data acquisition system of carbon fiber cement paste piezoresistive sensors. *Sensor. Actuat. A-Phys.*, 135: 360–369.

79. Shih, C.-J., Vijayaraghavan, A., Krishnan, R., Sharma, R., Han, J.-H., Ham, M.-H., Jin, Z., et al. (2011) Bi- and trilayer graphene solutions. *Nat. Nanotechnol.*, 6: 439–445.

80. Zheng, C., Fan, Z., Wei, T., and Luo, G. (2009) Temperature dependence of the conductivity behavior of graphite nanoplatelet-filled epoxy resin composites. *J. Appl. Polym. Sci.*, 113: 1515–1519.

81. Wang, W.-P., Liu, Y., Li, X.-X., and You, Y.-Z. (2006) Synthesis and characteristics of poly(methyl methacrylate)/expanded graphite nanocomposites. *J. Appl. Polym. Sci.*, 100: 1427–1431.
82. Zheng, G., Wu, J., Wang, W., and Pan, C. (2004) Characterizations of expanded graphite/polymer composites prepared by in situ polymerization. *Carbon*, 42: 2839–2847.
83. Wang, W.P., Pan, C.Y., and Wu, J.S. (2005) Electrical properties of expanded graphite/poly(styrene-co-acrylonitrile) composites. *J. Phys. Chem. Solids*, 66: 1695–1700.
84. Pramoda, K. P., Linh, N. T. T., Tang, P. S., Tjiu, W. C., Goh, S. H., and He, C. B. (2010) Thermomechanical properties of poly(vinylidene fluoride) modified graphite/poly(methyl methacrylate) nano composites. *Compos. Sci. Technol.*, 70: 578–583.