Graph-Theory-Based Quantification of Electro-Conductive Network Formation in Multilayer Graphene/Epoxy

H. Canché[1*], I. Isaac[1], O. Solís-Canto[2], A. Castillo-Atoche[3], F. Avilés[1]

[1] Unidad de Materiales, Centro de Investigación Científica de Yucatán, Mérida, Mexico, [2] Laboratorio Nacional de Nanotecnología, Centro de Investigación en Materiales Avanzados, Chihuahua, Mexico, [3] Laboratorio Robótica e Industria 4.0, Facultad de Ingeniería, Universidad Autónoma de Yucatán, Mérida, Mexico

**Corresponding author (helbert.canche@cicy.mx)*

Keywords: *Conductive network; graph theory; percolation; interconnectivity.*

1. Abstract

The development of electrically conductive polymer nanocomposites relies on the formation of a percolated filler network. However, establishing a quantitative link between macroscopic electrical properties and microscopic network morphology remains a significant challenge. This study proposes a novel methodology integrating optical microscopy imaging with graph-theory descriptors to quantitatively assess network interconnectivity. Multilayer graphene sheets/epoxy nanocomposites with filler loadings ranging from 1 to 8 wt.% were employed as a model system. Microscope optical images were analyzed through digital image processing, comprising binarization, morphological operators, and skeletonization algorithms. The skeleton network extracted from the microscopy images represents the underlying conductive architecture to convert the network into a graph, i.e., a set of nodes and edges. Through graph-theory analysis a set of network parameters are calculated from the graphs for the range of concentrations. Direct current electrical measurements as a function of the filler concentration yield the electrical percolation threshold at a weight fraction at 3.8 wt.%. Correlating these macroscopic results with microscopic network parameters demonstrated that the beta index and the global efficiency metrics act as highly sensitive topological indicators of the volumetric electrical conductivity. These parameters exhibited a strong correlation with the different regimens of the percolation curve, associated with microstructural interconnectivity from fragmented clusters to a continuously integrated network with redundant topological pathways. The average degree also closely mirrored this transition, whereas the network density proved to be a less representative metric. Ultimately, this experimental-theoretical approach establishes a direct, reproducible framework for quantifying structure-property relationship between the filler microstructural features of the network and the volumetric electrical conductivity, which can be extended to other polymer matrices, nanofillers, and effective properties governed by interconnectivity.

2. Introduction

Networks constitute a universal framework for describing interconnectivity in complex systems, and their structural analysis has proven essential across diverse scientific and technological fields [1]. Graph theory provides the formal mathematical background for such studies, enabling the abstraction of complex physical architectures into defined sets of nodes and edges, see Figure 1 [2].

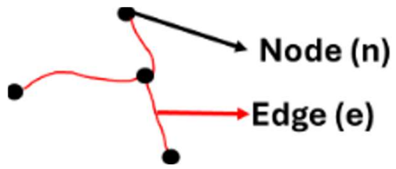


Figure 1. Graph representation of a network.

Within this theoretical framework, the specific topological arrangement and the interconnections of elements are related to the effective emergent properties and functional performance of the modeled systems. Consequently, graph-based approaches have been extensively utilized to quantify structural organization and functionality in disciplines ranging from biology to transportation and sociology [3–5]. In all these research fields, interconnectivity parameters provide a quantitative mechanism for linking underlying structure with emergent functionality, establishing graph theory as a versatile analytical tool. This analytical framework has been translated into the field of materials science to quantify microstructural interconnectivity. Foundational studies have successfully applied graph theory to evaluate microstructural features and correlate them with specific macroscopic behaviors, such as mechanical performance or general morphological organization [6]. In electrically insulating polymer materials, attaining macroscopic electrical conductivity requires the development of a continuous percolated structure incorporating conductive fillers, such as carbon nanomaterials [7,8]. These conductive polymer nanocomposites provide lightweight, corrosion-resistant, and mechanically robust solutions for electromagnetic interference shielding, wearable sensors, and structural health monitoring [9,10]. To optimize these advanced applications, a precise understanding of the topological architectures that dictate network connectivity, along with the correlation between this mesoscale microstructure and bulk effective properties, remains essential. Percolation theory has long been invoked to explain the sharp transition in electrical conductivity that occurs once a critical filler content is reached [11]. Nevertheless, the different variables associated with the electrical conductivity in nanocomposites (filler dispersion, aspect ratio, physicochemical properties of nanoparticles) make quantitative prediction highly challenging. To date, most approaches for studying conductive networks in nanocomposites have relied on theoretical and computational models. These include finite element simulations [12], statistical percolation theory [13], Monte Carlo simulations [14], and fractal analysis [15]. Although these models have provided fundamental insights, they often remain disconnected from the actual microstructural features observed in real, physically fabricated materials. Direct experimental quantification of network interconnectivity in materials science remains severely limited. This limitation is particularly evident at the mesoscale, a regime increasingly recognized as a significant factor in determining macroscopic properties of the material. To bridge this gap, this study proposes a novel methodology that integrates experimental microscopy imaging with graph theory and interconnection parameters to quantitatively assess interconnectivity in nanocomposite systems.

3. Materials and methodology

3.1 Materials and Nanocomposite Preparation

Commercial multilayer graphene sheets (GSs, XG Sciences, USA) with an average diameter of 16.7 µm, specific surface area of 144 m^2/g, and an average of 11 to 25 layers were used as the conductive filler. The matrix was a commercial bisphenol-A-based epoxy resin cross-linked with a polyoxypropylenediamine crosslinking agent modified with alkyl phenols at a 100:15 weight ratio. Nanocomposites were formulated with GS loadings from 1 to 8 wt.% in 1 wt.% increments. The GSs were incorporated into the epoxy and mechanically stirred at 50 °C for 15 minutes. To ensure optimal dispersion, the mixtures were processed using a three-roll mill with three consecutive passes. Roller gaps were set to 13 µm (feed) and 5 µm (output), with fixed speeds of 85, 180, and 369 rpm, respectively. The resulting nanocomposites were cured at room temperature for 12 hours, followed by a post-curing treatment in a convection oven for 6 hours at 65 °C, and an additional 6 hours at 95 °C. Specimens were cast as thin films (~25 µm) for optical microscopy and bulk rectangular bars (30×10×2 mm) for electrical characterization.

3.2 Digital Image Processing and Interconnectivity Quantification

Transmission micrographs were acquired using a SONY® XC-75 camera mounted on a LEICA DMLM optical microscope (Wetzlar, Germany). For each filler concentration, 100 images were captured at 10× magnification in 24-bit RGB format (640×480 pixels), yielding a calibrated scale of 2.08 µm/pixel. A custom-made Python program was developed to automate the extraction of the structural network through a sequential workflow.

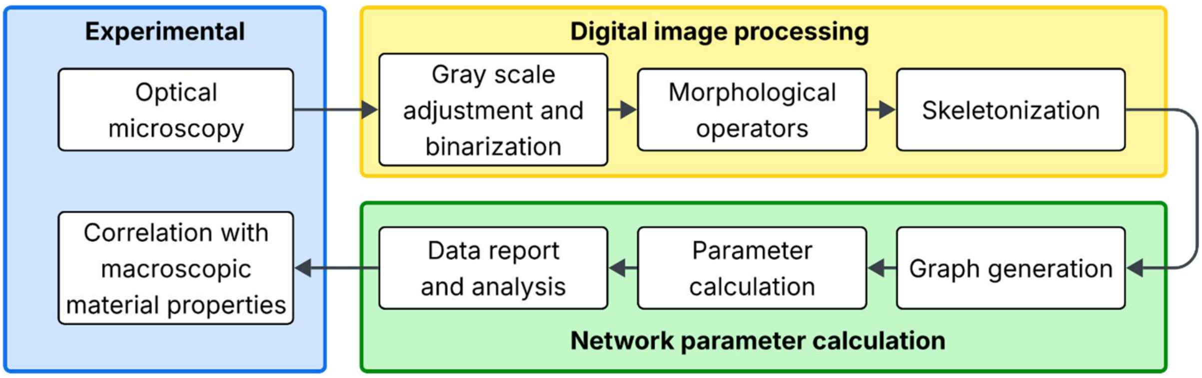


Figure 2. Workflow for the transformation of microscopic images into graph representations and their correlation to effective material properties.

The digital image processing uses a binarization process, utilizing grayscale conversion followed by Otsu's thresholding algorithm to isolate the conductive regions from the insulating matrix.

Subsequently, morphological operator "closing" was performed to refine the network. This operation comprises a dilation (increase contour by one pixel) followed by an erosion (decrease the contour one pixel) and is used to avoid overly small, isolated pixels and unphysical gaps in the image, cleaning the data from potentially spurious features. Following this algorithm, skeletonization was executed. The conductive domains were reduced to one-pixel-wide paths using Choi's Euclidean based algorithm [16], applying a distance threshold of 20 pixels to faithfully preserve the system's topological connectivity. To ensure statistical reliability, a representative area element analysis was performed. From the skeletonized images, the networks were modeled as graphs. Junctions were defined as nodes (*n*), and the conductive connections between them as edges (*e*), Fig. 1. This representation enabled the quantification of interconnectivity parameters studied in the graph theory field. A list of parameters was analyzed for this purpose. The parameters with a strong correlation with σ are summarized in Table 1.

Table 1. List of evaluated parameters.

Parameter	Equation	Description
Average degree ($\bar{k}$)	$\bar{k} = \sum_{i=0}^{i=n} \frac{k_i}{n_g}$	Arithmetic mean of the number of edges incident to each node within the graph.
Density (ρ_n)	$\rho_n = \frac{2e_g}{n_g(n_g-1)}$	Ratio between the number of existing edges and the maximum number of potential connections in a simple graph.
Global efficiency (G_e)	$G_e = \frac{1}{n_g(n_g-1)} \sum_{i=0\ (\neq j)}^{i=n-1} \frac{1}{L_n(i,j)}$	Average of the inverse shortest path distances between all pairs of nodes, representing the integration of the network.
Beta index (β)	$\beta = \frac{e_g}{n_g}$	Measure of network connectivity expressed as the ratio of the total number of edges to the total number of nodes.

n_g represents the number of nodes of the graph, e_g correspond to number edges in the graph, k_i is the grade of the node i, L_n (i,j) is the shortest longest path between node i and j.

3.3 Measurement of electrical conductivity

Direct current electrical resistance (*R*) was measured on the bulk specimens using a two-point probe configuration connected to a Keithley 6517B electrometer. Conductive paint was applied to the specimen edges to form parallel electrodes with a 20 mm span length. To minimize electrode polarization, an alternating polarity method was applied (±200 V reversed at 10 s intervals). The electrical conductivity (σ) was calculated as $\sigma = 1/(R \cdot s)$, where s is the cross-sectional area. The electrical conductivity data was fitted to the general effective media (GEM) model proposed by McLachlan [17],

$$\frac{(1-\phi^v)(\sigma_m^{\frac{1}{t}}-\sigma^{\frac{1}{t}})}{\sigma_m^{\frac{1}{t}}+\left(\frac{1-\phi_c^v}{\phi_c^v}\right)\sigma^{\frac{1}{t}}}+\frac{(\phi^v)(\sigma_f^{\frac{1}{t}}-\sigma^{\frac{1}{t}})}{\sigma_f^{\frac{1}{t}}+\left(\frac{1-\phi_c^v}{\phi_c^v}\right)\sigma^{\frac{1}{t}}}=0 \quad (1)$$

where σ_f and σ_m are the electrical conductivities of the filler and matrix, respectively. The adjustable parameter t accounts for phase morphology. The volume fractions (ϕ^v) and critical volume fractions (ϕ^v_c) were converted from the experimental weight concentrations using the manufacturer-provided densities for the GSs (2,200 kg/m³) and the epoxy polymer (1,150 kg/m³).

4. Results

4.1 Electrical conductivity and visualization of networks

The direct current electrical conductivity of the GS/epoxy nanocomposites was evaluated as a function of filler content to characterize the percolation behavior. Figure 3 presents the electrical conductivity for the GS/epoxy nanocomposite as a function of the filler volume concentrations.

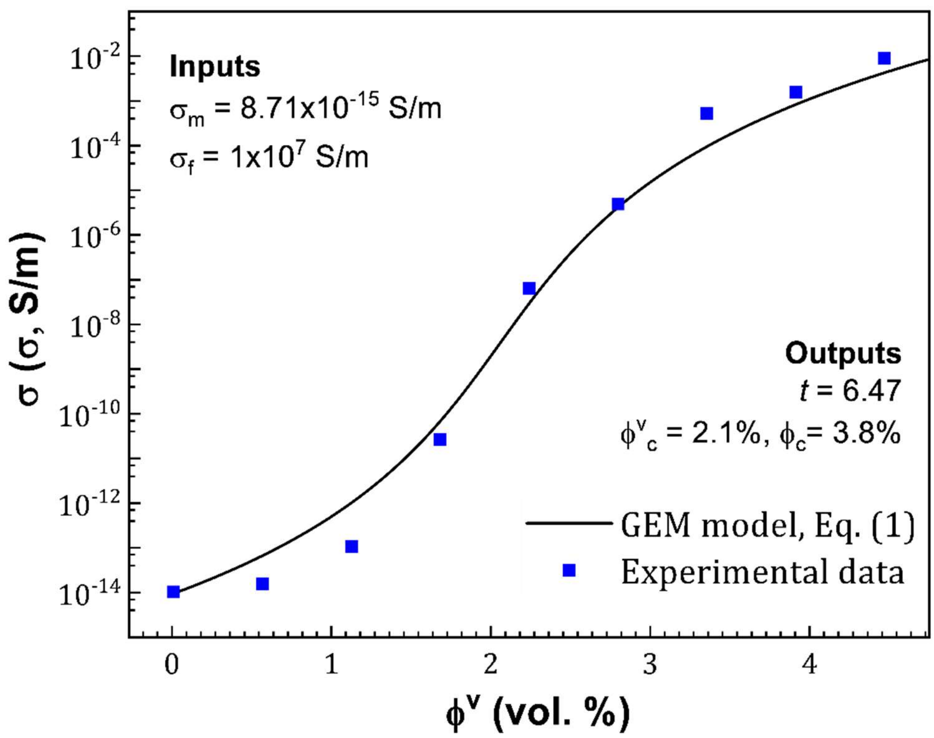


Figure 3. Measured electrical conductivity as function of the filler concentration fitted to the general effective media model.

The neat epoxy matrix behaved as a strong insulator with a conductivity on the order of 10^{-14} S/m. At low filler loadings (<3 wt.%), conductivity exhibited only a marginal increase, characteristic of a regime where the conductive fillers exist as isolated particles or disconnected clusters. A sharp insulator-to-conductor transition occurred in the narrow concentration range between 3 and 4 wt.%, where the conductivity abruptly surged by three to four orders of magnitude to approximately 10^{-4} S/m. This dramatic jump is associated with the electrical percolation threshold, indicating the formation of a continuously spanning network of interconnected graphenic sheets (GSs), which provide efficient pathways for macroscopic charge transport. Beyond 4 wt.%, the conductivity continued to increase at a more gradual rate as the established network densified. Fitting these experimental data to the GEM model accurately reproduced the transition trend across all filler concentrations, yielding a critical volume fraction of 2.1 vol.% (critical weight fraction of 3.8 wt.%). Furthermore, the model derived a value of 6.47 for the adjustable parameter t. In the context of effective media models, higher t values generally indicate a highly interconnected, continuous conductive morphology rather than a granular or poorly connected structure [18]. This mathematical fit supports the physical interpretation that the GS domains establish a well-integrated network above the threshold. Optical microscopy visually suggests these macroscopic transitions, see Figure 4.

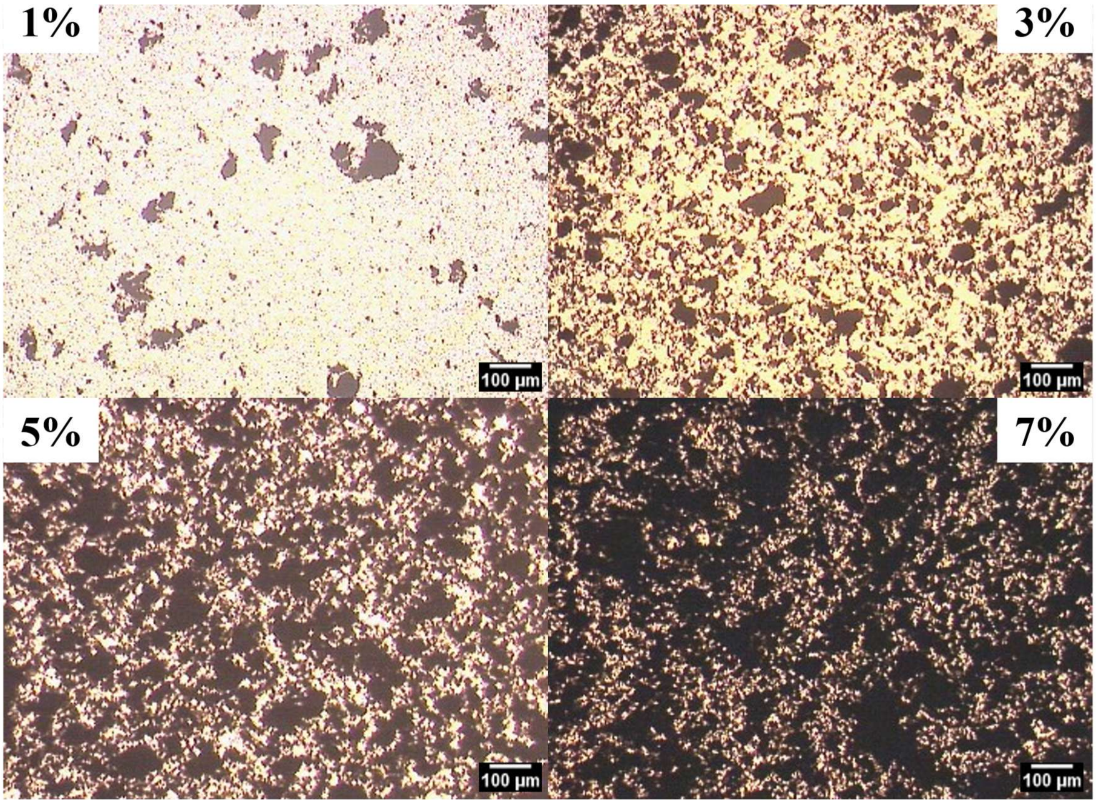
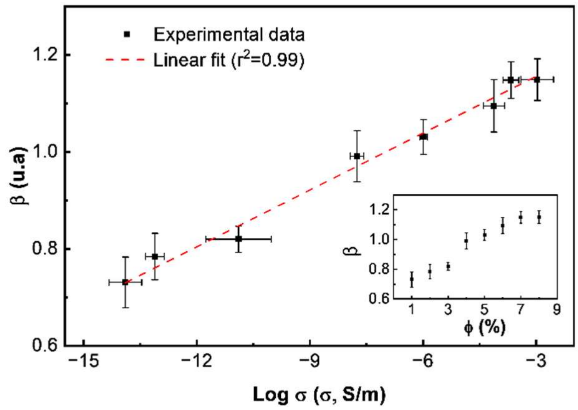


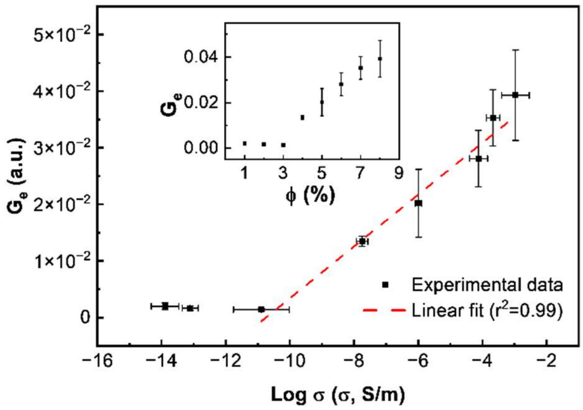
Figure 4. Optical microscopy images of the GS/epoxy composites at odd concentrations (1, 3, 5, 7 wt.%).

4.2 Correlation between microscopic interconnectivity parameters and macroscopic conductivity

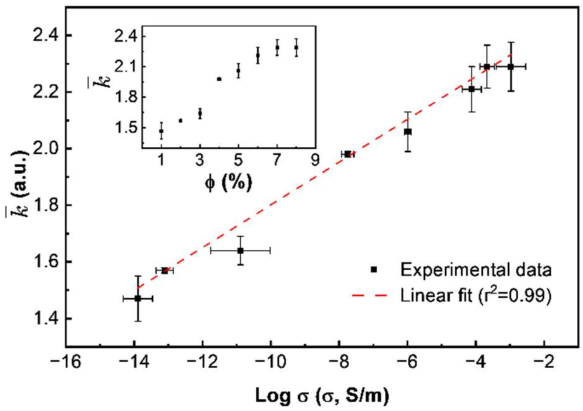
To quantitatively link these microstructural observations to the bulk material properties, graph-theory interconnectivity parameters were extracted from the microscopy data and correlated with the macroscopic electrical conductivity, see Figure 5. These parameters provide an analytical and quantitative framework for understanding physical connectivity. Among the evaluated metrics, the β index, global efficiency and average degree demonstrated the strongest structure-property correlations. Figure 5 shows the interconnected parameters as a function of electrical conductivity, with insets presenting the same parameters as a function of the filler weight concentration.



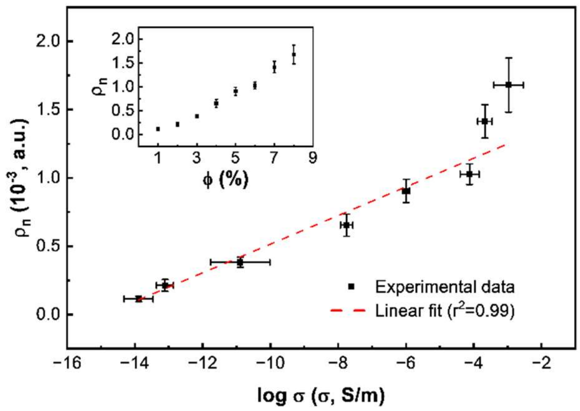
a)



b)



c)



d)

Figure 5. Network interconnectivity parameters plotted against electrical conductivity in logarithmic scale. Insets show plots against the filler concentration. a) Beta index, b) global efficiency, c) average degree, d) density.

In Figure 5a the β index, defined as the ratio of edges to nodes, is evaluated against the macroscopic electrical conductivity. The plot reveals a strong semi-logarithmic scaling with a linear fit (coefficient of determination, r^2 = 0.99), demonstrating that an incremental structural transition toward a connected state yields exponential enhancements in charge transport. For highly resistive states, corresponding to filler concentrations under 4 wt.% (see inset), the beta index remained below 1 for filler concentrations under 4 wt.%, accurately reflecting a sparsely connected network of isolated GS agglomerates with limited matrix connectivity [19]. In close relationship with the macroscopic percolation threshold, the β index exceeded 1 above 4 wt.%. This topological shift is associated with the transition from fragmented domains to a continuously integrated network. This suggests that the parameter can capture the interconnected pathways across the regimes of the percolation curve. Similarly, Figure 5b shows that the global efficiency at 1 and 2 wt.% remains in the low-conductivity regime (below 10^{-10} S/m), corresponding with global efficiency values near zero (see inset), indicating a lack of continuous conductive paths. Concurrent with the onset of electrical percolation (near 4 wt.%), the global efficiency sharply transitions into a robust semi-logarithmic linear fit (r^2 = 0.99). This correlation suggests that global efficiency effectively represents the efficiency of the electron transport through the nanocomposite network. The increment of global efficiency could be explained as the increment of redundant parallel routes that actively participate in macroscopic electron mobility [20]. Figure 5c highlights the linear correlation between the electrical conductivity and the average degree of the network in a semi-log plot. In foundational two-dimensional lattice percolation models, an average degree of 2 represents a critical threshold for network robustness [21]. Here, the linear fit reveals that crossing this localized threshold (surpassing a value of 2 near the 4 wt.% mark, see inset) correlates precisely with the composite reaching its highest conductive states. An average degree greater than 2 confirms that individual nodes are increasingly participating in multiple conductive pathways. The logarithmic scaling proves that creating just a few highly branched, localized connections exponentially facilitates the widespread distribution of charge carriers. Figure 5d reveals the limitations of the density parameter. While it exhibits a general linear correlation (r^2=0.99) with σ, the data points at the highest conductivity values visibly deviate and spike above the linear fit. Furthermore, the density parameter shows a continuous, gradual increase as a function of filler concentration from the very beginning (see inset), failing to reflect the abrupt insulating-to-conducting transition seen in the other parameters. Analyses of other complex systems, such as urban infrastructure networks, report that an increase in global density does not necessarily equate to proportional functional enhancements [22]. As the nanocomposite network expands at high filler loadings, the mathematical incorporation of new nodes dilutes the functional impact of new connections, resulting in diminishing returns for macroscopic conductivity and rendering density a less sensitive descriptor for charge transport efficiency.

5. Conclusions

This study evaluated the application of graph theory as a novel framework for characterizing microstructural interconnectivity in conductive polymer nanocomposites. By integrating macroscopic electrical conductivity measurements with digital image processing, direct structural-property correlations were established for a multilayer graphene/epoxy system. The extraction of skeletonized graphs from optical micrographs successfully translated complex physical microstructures into measurable networks, allowing for the precise tracking of structural evolution from isolated domains to continuous conductive architecture. Among the evaluated graph theory metrics, the beta index, global efficiency and average degree emerged as the most sensitive and accurate indicators of the insulator-to-conductor transition. They strongly correlated with the macroscopic electrical response, capturing the critical emergence of interconnected, redundant pathways necessary for continuous electron mobility near the 3.8 wt.% percolation threshold. This aligns with fundamental percolation models and confirms that individual nodes increasingly participate in multiple conductive routes to facilitate efficient charge distribution. Conversely, metrics such as the density exhibited a progressive, gradual increase that failed to capture the abrupt functional enhancements of the percolation transition. This highlights that simple spatial occupation does not perfectly equate to optimized transport efficiency. Ultimately, this methodology offers a highly reproducible approach to analyzing nanostructured networks exactly as they are physically realized within polymer composites, providing a versatile tool for the future design and optimization of functional materials.

6. References

[1] M. Barthelemy. "Spatial Networks". In: Encyclopedia of Social Network Analysis and Mining, 2nd edition, Springer New York, pp 1967-1976, 2018.

[2] R.J. Wilson. "Introduction to Graph Theory". 5th edition, Prentice Hall, Harlow, UK, 2010.

[3] F.V. Farahani, W. Karwowski and N.R. Lighthall. "Application of graph theory for identifying connectivity patterns in human brain networks: A systematic review". Front. Neurosci., Vol. 13, pp 585, 2019.

[4] A. Sevtsuk and R. Kalvo. "Modeling pedestrian activity in cities with urban network analysis". Environ. Plan. B Urban Anal. City Sci., Vol. 52, pp 377-395, 2025.

[5] Z.D. Kenger, Ö.N. Kenger and E. Özceylan. "Analytic hierarchy process for urban transportation: a bibliometric and social network analysis". Cent. Eur. J. Oper. Res., Vol. 33, pp 1005-1024, 2025.

[6] D.A. Vecchio, S.H. Mahler, M.D. Hammig and N.A. Kotov. "Structural Analysis of Nanoscale Network Materials Using Graph Theory". ACS Nano, Vol. 15, pp 12847-12859, 2021.

[7] A.J. Marsden, D.G. Papageorgiou, C. Vallés, A. Liscio, V. Palermo, M.A. Bissett, R.J. Young and I.A. Kinloch. "Electrical percolation in graphene–polymer composites". 2D Mater., Vol. 5, pp 032003, 2018.

[8] R. Taherian. "Experimental and analytical model for the electrical conductivity of polymer-based nanocomposites". Compos. Sci. Technol., Vol. 123, pp 17-31, 2016.

[9] A.I.J. Alqaderi and N. Ramakrishnan. "Carbon-based flexible strain sensors: Recent advances and performance insights in human motion detection". Chem. Eng. J., Vol. 513, pp 162609, 2025.

[10] S. Yuan, J. Deng and L. Li. "Manipulating 2D Nanomaterials: Shaping the Future of Intelligent Wearable Health Monitoring Devices". ACS Nano, 2026.

[11] S. Kirkpatrick. "Percolation and Conduction". Rev. Mod. Phys., Vol. 45, pp 574-588, 1973.

[12] M. Khamehchi, Z. Zhao, M.J. Mahmoodi, Z. Wang and F. Narita. "The electrical resistivity of CB–polymer piezoelectric hybrid nanocomposites: Experimental and micromechanical studies". Compos. Sci. Technol., Vol. 276, pp 111504, 2026.

[13] M. Soto, M. Esteva, O. Martínez-Romero, J. Baez and A. Elías-Zúñiga. "Modeling percolation in polymer nanocomposites by stochastic microstructuring". Materials, Vol. 8, pp 6697-6718, 2015. [14] Z. Zabihi and H. Araghi. "Monte Carlo simulations of effective electrical

conductivity of graphene/poly(methyl methacrylate) nanocomposite: Landauer-Buttiker approach". Synth. Met., Vol. 217, pp 87-93, 2016.

[15] K.M. Jäger and D.H. McQueen. "Fractal agglomerates and electrical conductivity in carbon black polymer composites". Polymer, Vol. 42, pp 9575-9581, 2001.

[16] W.-P. Choi, K.-M. Lam and W.-C. Siu. "Extraction of the Euclidean skeleton based on a connectivity criterion". Pattern Recognition, 2003.

[17] D.S. McLachlan. "An equation for the conductivity of binary mixtures with anisotropic grain structures". J. Phys. C: Solid State Phys., Vol. 20, pp 865-877, 1987.

[18] D.S. McLachlan and G. Sauti. "The AC and DC conductivity of nanocomposites". J. Nanomater., Vol. 2007, pp 30389, 2007.

[19] K. Kansky and P. Danscoine. "Measures of network structure". Flux, Vol. 5, pp 89-121, 1989.

[20] S. Achard and E. Bullmore. "Efficiency and cost of economical brain functional networks". PLoS Comput. Biol., Vol. 3, pp 0174-0183, 2007.

[21] R.G. Larson, L.E. Scriven and H.T. Davis. "Percolation theory of two phase flow in porous media". Chem. Eng. Sci., Vol. 36, pp 57-73, 1981.

[22] S. Wang, D. Yu, M.P. Kwan, L. Zheng, H. Miao and Y. Li. "The impacts of road network density on motor vehicle travel: An empirical study of Chinese cities based on network theory". Transp. Res. Part A Policy Pract., Vol. 132, pp 144-156, 2020.