Examining the contribution of factors affecting the electrical behavior of poly(methyl methacrylate)/graphene nanoplatelets composites

Xiaoling Luo1 | Dirk W. Schubert1,2

1Institute of Polymer Materials, Friedrich-Alexander-University Erlangen-Nuremberg, Erlangen, Germany
2KeyLab Advanced Fiber Technology, Bavarian Polymer Institute, Fürth, Germany

Correspondence
Xiaoling Luo, Institute of Polymer Materials, Friedrich-Alexander-University Erlangen-Nuremberg, Martenstr. 7, Erlangen 91058, Germany.
Email: xiaoling.luo@fau.de

Abstract
In this study, poly(methyl methacrylate) (PMMA)/graphene nanoplatelets (GNPs) conductive composite films with different morphologies were fabricated from the same constituent materials using four fabrication techniques, solution casting (SC), SC followed by hot pressing (SCP), melt mixing followed by SC (MSC), and melt mixing followed by hot pressing (MP). Morphologies of dispersed GNPs and electrical properties in both in-plane and perpendicular direction were investigated and compared systematically. The corresponding percolation thresholds ($\Phi_c$) of the composites varied from 0.42 ± 0.13 vol% to 3.26 ± 0.48 vol%. The conductivities varied up to two orders of magnitude and decreased in the sequence of SC > MSC > SCP > MP. These variations were explained in terms of GNPs size, GNPs orientation, distribution and dispersion state of fillers. The contribution of the above factors in each procedure were discerned individually, the results were discussed and compared with other experimental studies and simulations as well.

KEYWORDS
films, morphology, nanostructured polymers, nanotubes, graphene and fullerenes, theory and modeling

1 | INTRODUCTION

The incorporation of conductive fillers into nonconductive polymer matrices allows to obtain a new class of electrically conductive polymer composites (CPCs). Traditional carbon-based fillers such as carbon nanotubes and carbon black make excellent candidates for conductive composites. While low percolation thresholds have been observed, achieving a high ultimate conductivity requires a greater loading of filler, and this often makes the composite brittle. Therefore, graphene has attracted significant scientific attention as a potential alternative conductive filler. Graphene is a two-dimensional sheet of carbon atoms, $sp^2$-bonded into a hexagonal arrangement. It has an exciting combination of properties, especially its superb electrical conductivity (up to $10^6$ S m$^{-1}$). There is now a family of graphene-related materials, such as pristine graphene, graphene oxide, reduced graphene oxide, and graphene nanoplatelets (GNPs). Typically, GNPs are much cheaper than other forms of graphene and are commercially available on the tonne scale.

The effects of filler orientation on the conductivity of the composite have been extensively studied recently, and anisotropic electrical properties have been reported. The orientation of fillers could happen by using...
conventional manufacturing methods, novel manufacturing methods, or applying an external electric or magnetic field. Wu et al. found the compression molded samples showed slightly orientation of graphene and higher electrical conductivity with respect to the injection molded ones. For compressed samples, the in-plane percolation threshold ($\Phi_c$) was around 1 wt% and the perpendicular $\Phi_c$ was 3 wt%. For injected samples, the in-plane $\Phi_c$ was 10 wt% while that of perpendicular direction was higher. Wang et al. prepared graphene aerogels using a novel unidirectional freeze casting method, the obtained highly aligned, porous structure of aerogels caused over an order of magnitude difference in conductivity of epoxy composite. Wu et al. used electric field to align graphene in an epoxy polymer, the conductivity of the CPCs in the alignment direction of the graphene was consistently 2–3 orders of magnitude higher than both that along the transverse direction and that of the CPCs containing randomly oriented graphene. The corresponding $\Phi_c$ were 0.22 and 0.52 vol% for CPCs with aligned graphene and randomly oriented graphene, respectively. However, few of these studies reported the effect of other factors in addition to filler orientation, such as shape and size of fillers, polymer–filler interactions, dispersion and distribution state of fillers.

If the fillers have a large contact surface and aspect ratio, the nanostructures make it possible to form conducting networks much more efficiently than fillers with a spherical shape. Stronger interfacial interactions or ducting networks much more efficiently than fillers with ratio, the nanostructures make it possible to form con- action, dispersion and distribution state of fillers. Wu et al. reported the effect of other factors in addition to filler orientation, such as shape and size of fillers, polymer–filler interactions, dispersion and distribution state of fillers.

EXPERIMENTAL

Materials and sample preparation

The matrix material was PMMA Plexiglas 7 N (Evonik Röhm GmbH, Germany), with $M_w$ = 99 kg/mol and polydispersity index = 1.52. Tetrahydrofuran (THF) was obtained from Sigma Aldrich, Saint Louis, MO, USA. GNP were supplied by ProGraphite GmbH, Germany, with about 10 layers, d$_{50}$ of 50 μm and conductivity of 800–1100 S cm$^{-1}$.

All materials were dried at 80°C in a vacuum oven for at least 12 h prior to processing. As shown in Figure 1, the PMMA/GNP composites were prepared via solution mixing and melt mixing, the films were fabricated via casting and hot pressing. The solution mixing was carried out under ambient conditions (around 23°C, 55% RH). GNP of various loading were sonicated in THF for 30 min to yield a homogeneous dispersion, and then PMMA pellets were added into the GNP/THF suspensions. The concentration of polymers was kept at about 4 wt% in this work. The final concentration of GNP in PMMA/GNP composites was from 0.3 to 4.0 vol%. Next, the PMMA/GNP/THF mixtures above were stirred 24 h. Finally, these mixtures were cast onto glass plates and dried under ambient conditions for 48 h (SC sample). Further hot press on the SC sample was employed under vacuum at a temperature of 200°C and a pressure of 200 bar for 5 min (SCP sample). For melt mixing, GNP and PMMA were mixed in an internal kneader PolyDrive (Haake, type 557-8310) at a temperature of 200°C and a
rotation speed of 60 min\(^{-1}\) for 10 min. The designed GNPs fractions were from 0.5 to 5.0 vol\%. After granulation, the pellets were dissolved into THF followed by casting (MSC sample) or were hot pressed into films (MP sample). The thickness of all the samples was controlled to be about 0.2 mm.

### 2.2 Characterization

The actual GNPs weight fractions of the melt mixed composites were determined by thermogravimetric analysis (TGA) under a nitrogen atmosphere, with a heating rate of 10\(^{\circ}\)C/min. The relationship between GNPs volume fractions and weight fraction can be described by Equation (1),

\[
\text{vol} = \frac{\text{wt}/\rho_{\text{GNPs}}}{\text{wt}/\rho_{\text{GNPs}} + (1-\text{wt})/\rho_{\text{PMMA}}},
\]

where \(\rho_{\text{GNPs}} = 2.2 \text{ g cm}^{-3}\) and \(\rho_{\text{PMMA}} = 1.19 \text{ g cm}^{-3}\). The result of TGA is shown in Figure S1. Sample code, volume fraction as well as weight fraction of GNPs are summarized in Table 1.

**TABLE 1** PMMA/GNPs composite formulations

| Sample code | GNPs volume fraction vol% | GNPs weight fraction wt% | Sample code | GNPs volume fraction vol% | GNPs weight fraction wt% |
|-------------|---------------------------|--------------------------|-------------|---------------------------|--------------------------|
| SC 0.4      | 0.4                       | 0.7                      | SCP 0.5     | 0.5                       | 0.9                      |
| SC 0.5      | 0.5                       | 0.9                      | SCP 0.8     | 0.8                       | 1.5                      |
| SC 0.8      | 0.8                       | 1.5                      | SCP 1.0     | 1.0                       | 1.8                      |
| SC 1.0      | 1.0                       | 1.8                      | SCP 2.0     | 2.0                       | 3.6                      |
| SC 1.5      | 1.5                       | 2.7                      | SCP 3.0     | 3.0                       | 5.4                      |
| SC 2.0      | 2.0                       | 3.6                      | SCP 4.0     | 4.0                       | 7.2                      |
| MSC 0.5     | 0.5                       | 0.9                      | MP 0.9      | 0.9                       | 1.6                      |
| MSC 0.9     | 0.9                       | 1.6                      | MP 1.9      | 1.9                       | 3.5                      |
| MSC 1.9     | 1.9                       | 3.5                      | MP 2.6      | 2.6                       | 4.7                      |
| MSC 2.6     | 2.6                       | 4.7                      | MP 3.0      | 3.0                       | 5.4                      |
| MSC 3.0     | 3.0                       | 5.4                      | MP 3.3      | 3.3                       | 6                        |
| MSC 3.3     | 3.3                       | 6                        | MP 3.9      | 3.9                       | 6.9                      |
| MSC 3.9     | 3.9                       | 6.9                      | MP 4.6      | 4.6                       | 8.2                      |
| MSC 4.6     | 4.6                       | 8.2                      |

Abbreviations: GNP, graphene nanoplatelets; MP, melt mixing followed by hot pressing; MSC, melt mixing followed by SC; PMMA, poly(methyl methacrylate); SC, solution casting, SCP, SC followed by hot pressing.
Investigation of the macro-scale distribution of GNP s in PMMA matrix was observed with an optical microscopy (OM) (Leitz, Orthoplan P). To determine the geometrical size of GNP s in the composites, samples were redissolved in THF to form dilute solutions, followed by casting on glass plates and observing with the light microscope. The images obtained were then analyzed using the JMicrovision image analysis freeware. At least 500 GNP s per concentration were measured.

Scanning electron microscopy (SEM) (Carl Zeiss Microscopy, Germany) was conducted to investigate the morphologies of the composite films, operating at an accelerating voltage of 3 KV. The composite films were previously fractured at room temperature and the cross-sections were coated with a gold layer using Sputter Coater S150B from Edwards.

The electrical resistances $R$ of composites both in in-plane direction and through-plane direction were measured under ambient temperature and humidity (around 23°C, 55% RH), using a Keithley 6487 Pico ammeter at a constant voltage (1 V) based on a homemade setup as shown in Figure 2. The electrical conductivity $\sigma$ was then calculated as:

$$\sigma = \frac{d}{(R \times S)}, \quad (2)$$

where $R$ is the electrical resistance of the sample, $d$ is the length of the sample parallel to the direction of the voltage or the distance between two electrodes, $S$ is the area of the sample perpendicular to the direction of the voltage.

### 3 | RESULTS AND DISCUSSION

#### 3.1 | GNP s size

The OM image and lateral area distribution of as received GNP s and GNP s in composites prepared from different routes are shown in Figure 3. The uncertainty $\Delta$ represents the 95% confidence interval for the GNP s size.

$$\Delta = \pm \frac{1.96 \times SD}{\sqrt{N}}, \quad (3)$$

where $N$ is the number of units studied, $N \geq 500$ in this work, taking from five images for five samples. SD is the standard deviation.

As shown in Figure 3(a), the as-received GNP s had an average lateral size of 1137 $\mu$m$^2$ with the most size between 200 and 400 $\mu$m$^2$. Regarding GNP s as circles, an average diameter of 38 $\mu$m could be obtained. The size of GNP s in SC 2.0 sample (Figure 3(b')) was comparable while that in MSC 1.9, SCP 2.0, and MP 1.9 sample (Figure 3(d'), (e')) showed obvious smaller size. This indicates that SC method preserved the GNP s better while the GNP s could be efficiently broken up during melt compounding with the PMMA matrix or during the hot pressing. In other words, simple mechanical shearing at molten state can facilitate the exfoliation of the GNP s into smaller dimension. The size reduction presumably caused by the interaction of GNP s-PMMA, interaction of GNP s-GNP s and processing equipment surfaces.

In order to investigate the relation between GNP s size and GNP s content, GNP s size of composites with various filler loading was also measured and the mean values are shown in Figure 4. For SC composites, SC 0.5 had a size of 1178 ± 124 $\mu$m$^2$, and all showed negligible difference at different concentration. The slight increasement at 3.0 vol% (1281 ± 152 $\mu$m$^2$) might be ascribed to the formation of some agglomerations of GNP s as the concentration increased. Interestingly, in the case of MSC sample the rise became more remarkable. As GNP s concentration increased from 0.9 to 3.9 vol%, the size of GNP s increased from 522 ± 60 $\mu$m$^2$ to 868 ± 180 $\mu$m$^2$. Presumably some agglomerations of GNP s also formed at higher GNP s concentration during melt compounding, which could not be completely broken when dissolved. SCP sample had a
similar size of GNPs \( (1110 \pm 163 \, \mu m^2) \) to SC sample at a content of 0.5 vol\%, which dropped to 681 \( \pm 71 \, \mu m^2 \) as it increased to 1.0 vol\% and almost kept constant with further loading increasing. Unlike MSC sample, with GNPs increasing, the size of GNPs of MP composites decreased from 613 \( \pm 83 \, \mu m^2 \) (0.9 vol\%) to 550 \( \pm 81 \, \mu m^2 \) (3.9 vol\%). The reduction of GNPs size in SCP and MP sample could be attributed to the interaction of GNPs-PMMA and GNPs-GNPs improving due to more steric hindrance imposed by more particles during the compression process.\(^{59}\)

### 3.2 Distribution, dispersion and orientation of GNPs in the PMMA matrix

The surface of the composite films prepared with four different processing methods was observed with optical microscopy. Figure 5 shows macroscopic distribution levels of GNPs in the composite samples in the in-plane direction. Strong surface segregation of GNPs in transparent PMMA matrix was evident in the case of the SC and MSC sample while that in SCP and MP sample was not observed. Thus, this phase separated morphology appears to have been induced during the SC process, independent on the compounding method. During solvent evaporation, the intrinsic incompatibility between GNPs and PMMA may drive the segregating process.\(^{60}\) On the contrary, SCP and MP samples showed well-distributed GNPs due to the shear forces during compression.\(^{61}\)

The morphologies of the cross-section of composite films were observed with SEM and the result is shown in Figure 6. The distribution at micro-scale of GNPs through the thickness is clearly demonstrated. Some isolated graphene clusters could be discerned as shown by the rough parts in the images. In Figure 6(a), MSC 1.9 showed layered structure with upper PMMA-rich layer and under GNPs-rich layer. The layered structure indicates a poor compatibility between GNPs and matrix in a solution state. The loss of compatibility relative to SC sample might be attributed to the high temperature or shearing during melt mixing. With poor compatibility with matrix, most GNPs were deposited toward the bottom due to the gravity effect.\(^{62}\) As the GNPs content increased to 3.9 vol\% (Figure 6(b)), the polymer layer became thinner. For SC, MP samples (Figure S2) and SCP samples (Figure 6(c), (d)), this layered structure did not occur, indicating better compatibility between the matrix and fillers.

It can also be seen from Figure 6 that most of the GNPs tended to orient along the in-plane direction for all samples. Besides, the level of the GNPs orientation varied with the GNPs concentration. As shown in Figure 6(d),...
the alignment of GNPs along in-plane direction in SCP 4.0 was more severe than that in SCP 3.0 (Figure 6(c)). This self-alignment phenomenon could be explained by the steric hindrance and $\pi-\pi$ interactions between the GNPs as well as the excluded volume concept.\textsuperscript{27,28}

High magnification SEM images of composite films are displayed in Figure 7, further demonstrating the GNPs dispersion at nano-scale (or exfoliation) for the four different processing methods in detail. SC 2.0 sample (Figure 7(a)) had large zones covered by loose GNPs flakes and had homogeneous dispersion. In Figure 7(b), several GNPs flakes stacking together is visible for MSC 1.9 due to the abovementioned layered structure. Similarly, SCP 2.0 (Figure 7(c)) also shows tighter stacks of GNPs, while MP 1.9 (Figure 7(d)) shows tightest and least homogeneous GNPs clusters. This is due to strong $\pi-\pi$ bonding between graphene layers without solvent-aided dispersion, as a result, large parts of PMMA matrix can be seen from the image.\textsuperscript{63,64} From the findings, it is considered that SC process had the best exfoliation of GNPs. It should be noted that the distribution, dispersion and exfoliation are different terms to describe graphene states. “Distribution” describes the way the individual sheets or their agglomerates fill the matrix at micro- and macroscopic scales. “Dispersion”
indicates GNPs are agglomerated or not, dispersion at nano-scale reflects the "exfoliation" or "stacking" state of graphene sheets in the matrix. For CPCs, the ideal state of fillers in the matrix is bad distribution and good dispersion. The conductive network can easily form from bad distribution due to the high concentration of conductive particles in a local position such as the segregation in SC and MSC sample, while the good dispersion means more conductive particles can be released from the filler aggregates to construct conductive network. The summary of the results of morphology analysis was listed in Table 2.

### 3.3 Electrical conductivity and percolation behavior

The electrical conductivity of CPCs is strongly dependent on the volume fraction of conductive fillers. Percolation threshold ($\Phi_c$) is a certain concentration at which the electrical conductivity of CPCs increases by several orders of magnitude and the insulator/conductor transition is achieved in the percolation process. Based on the conductivity data, McLachlan’s general effective medium (GEM) equation was found to be able to describe successfully the conductivity data in a broad range of filler concentrations, that is, below and above $\Phi_c$ as well as the transition region, for many conductive composites. This equation is as follows:

\[
\frac{1 - \Phi}{\sigma_m - \sigma_c} \cdot \left( \frac{\sigma_c}{\sigma_m + \frac{1}{\Phi_c - \sigma_c}} \right) + \Phi \frac{\sigma_f - \sigma_c}{\sigma_f + \frac{1 - \Phi}{\Phi_c - \sigma_c}} = 0, \quad (4)
\]

where $\sigma_m$, $\sigma_c$, $\sigma_f$ are the conductivities of the PMMA matrix, the composite and the GNPs, respectively. $\Phi$ is the volume fraction of fillers and $\Phi_c$ is the percolation threshold.
threshold. The values of the exponent \( s \) and \( t \) are generally taken to be 0.87 and 2, respectively.

The GEM Equation (4) was used to obtain the percolation threshold \( \Phi_c \). \( \sigma_m \) (2.28 \times 10^{-13} \text{ S cm}^{-1}) was measured on a pure PMMA film cast or compressed under the same conditions as the other samples. \( \sigma_f \) is 800–1100 S cm\(^{-1}\) stated by the manufacturer. The experimental conductivity data in both in-plane (denoted as -I) and perpendicular direction (denoted as -P) as a function of GNPs volume fraction were described. Total of 9 measurements were conducted to obtain the mean conductivity and standard deviation as shown by vertical error bars. As shown in Figure 8, the theoretically calculated conductivities (dashed lines) were close to the experimentally determined conductivities (points).

Based on the geometry of conductive fillers, Li and Jim\(^6\) developed an analytical model based on average interparticle distance (IPD) approach to predict the percolation threshold of polymer nanocomposites containing 3D randomly distributed disc-shaped nano particles.

The equation is given as:

\[
\Phi_c = \frac{27\pi D^2 t}{4(D + D_{IP})^3},
\]

where \( t \) is the filler thickness, \( D \) is the filler diameter, and \( D_{IP} \) denotes the IPD. The critical \( D_{IP} \) values are varied between 10 nm and 1 \( \mu \text{m} \), the effect of \( D_{IP} \) criterion on percolation threshold becomes negligible as far as the aspect ratio is high enough (i.e., \( D/t \geq \) about 500).

It has been confirmed that the theoretical \( \Phi_c \) value calculated from Equation (5) was in accordance to the determined \( \Phi_c \) by considering a proper average lateral dimension and thickness of GNPs.\(^6\) In this work, \( \Phi_c \) generated from GEM Equation (4) is regarded as experimental data and is listed in Table 3. Equation (5) yields the dependence of \( \Phi_c \) on the diameter \( D \), thickness \( t \), and IPD by considering the GNPs 3D randomly distributed. \( D \) was between 25 and 40 \( \mu \text{m} \) for composites prepared with different methods (calculated from Section 3.1). If GNPs distributed without any further exfoliation or stacking as received, then \( t \) could be considered 3.35 nm (interlayer space: 0.335 nm, 10 layers) as stated by the manufacturer. Here, the \( D/t \geq 500 \), \( D_{IP} \) can be neglected mathematically. As an isotropic GNPs orientated system, the model predicts a \( \Phi_c \) between 0.18 and 0.28 vol%.

It is noted that the experimental \( \Phi_c \) were all higher than that predicted from Equation (4). This reveals the discrepancy between the experimental system and the ideal model based on randomly distributed GNPs. A major reason is, the actual GNPs thickness would be larger than 3.35 nm used for predicting \( \Phi_c \), as the stacked GNPs flakes shown in the SEM images, and the thickening of GNPs flakes increased \( \Phi_c \). Although the actual thickness of each case cannot be speculated simply with Equation (5) since there were other differences in the morphology of composites between the model and experiment, the relationship between \( \Phi_c \) and GNPs diameter and GNPs thickness could further help investigate the contribution of GNPs size and GNPs stacking in the following sections.

**FIGURE 8** Logarithm of the conductivity (log \( \sigma \)) in (a) in-plane direction and (b) perpendicular direction as a function of graphene nanoplatelets (GNPs) volume fraction. The dashed lines show the best fit utilizing equation (4) [Color figure can be viewed at wileyonlinelibrary.com]
TABLE 3 $\Phi_c$ (vol%) of different samples in in-plane and perpendicular direction

| Sample | SC     | MSC    | SCP    | MP     |
|--------|--------|--------|--------|--------|
| In-plane| 0.80 ± 0.25 | 0.67 ± 0.11 | 2.00 ± 0.03 | 3.26 ± 0.48 |
| Perpendicular| 0.42 ± 0.13 | 0.77 ± 0.18 | 0.89 ± 0.16 | 2.33 ± 0.53 |

Abbreviations: MP, melt mixing followed by hot pressing; MSC, melt mixing followed by SC; SC, solution casting, SCP, SC followed by hot pressing.

3.4 Contribution of GNPs size and layered structure to the electrical properties

Considering GNPs size and layered structure in MSC sample as the two main factors determining the electrical conductivities and percolation behaviors of SC and MSC sample, differences between them could be explained. As demonstrated by Equation (5), the composite with a larger diameter has lower percolation threshold. In the simulated result of PMMA/GNPs composite by Zabihi and Araghi, lower percolation threshold as well as lower conductivity were also obtained for larger GNPs. In agreement with the simulations, SC sample with larger GNPs had a lower $\Phi_{c,P}$ ($0.42 \pm 0.13$ vol%) than MSC sample ($0.77 \pm 0.18$ vol%). Besides, a lower log $\sigma_I$ was also found for SC sample. However, the conductive behavior of MSC sample was also influenced by the layered structure. Only if GNPs formed a percolated network in the top PMMA-rich layer, the perpendicular direction started to conduct.

That is another reason why MSC sample had a greater $\Phi_{c,P}$ than SC sample. Similarly, the log $\sigma_P$ of MSC sample was lower than that of SC sample at the beginning but approached that of SC sample as the concentration of GNPs increased to 3.0 vol% since the matrix-rich layer got thinner. It seems the effect of layered structure dominated this process.

On the other hand, more conductive paths in the in-plane direction would be formed in the bottom area compared to uniformly dispersed systems. This is another factor leading to a higher log $\sigma_I$ of MSC sample in addition to their smaller filler size. Similarly, a smaller amount of GNPs would be required to achieve percolation threshold since it became conductive as long as the bottom GNPs-rich layer percolated. As a result of the competition between positive effect of layered structure and negative effect of smaller GNPs size, MSC sample eventually had a slightly lower $\Phi_{c,I}$ ($0.67 \pm 0.11$ vol%) than SC sample ($0.8 \pm 0.25$ vol%). This finding also indicates that the difference in GNPs size had less significant influence on the electrical properties of composites than layering effect.

3.5 Contribution of the segregation of GNPs to the electrical properties

Comparing the percolation thresholds of SC and SCP composites, $\Phi_{c,I}$ and $\Phi_{c,P}$ of SC sample were $0.8 \pm 0.25$ vol% and $0.42 \pm 0.13$ vol%, respectively, while those of SCP sample were $2 \pm 0.03$ vol% and $0.89 \pm 0.16$ vol%, respectively. In addition to the difference in GNPs size which has less profound impact on the electrical properties, this could be mainly explained by the segregation of GNPs in the SC sample, which disappeared after hot pressing for SCP sample. In other words, the phase segregation effect reduced $\Phi_{c,I}$ and $\Phi_{c,P}$ of about 1.2 and 0.47 vol%, respectively. This indicates that GNPs segregation was a benefit for conductive network, facilitating the percolating process at lower amount of GNPs. It could also be concluded that it had a more significant promotion effect on the formation of conductive pathways in in-plane direction. With respect to the electrical conductivity of SC and SCP sample (when $\Phi > \Phi_c$), both log $\sigma_I$ and log $\sigma_P$ of SC sample were about one order of magnitude higher than those of SCP sample, and the difference between them remained almost the same as the GNPs content increased. Here the segregation of GNPs means a poor distribution resulting from the incompatibility between matrix and fillers. The better electrical properties due to this poor distribution was in agreement with some literatures where a slight increase in $\Phi_c$ was observed as the compatibilization method applied. This is ascribed to an increased number of individually dispersed platelets and a loss of interconnectivity.

3.6 Contribution of the stacking of GNPs to the electrical properties

In comparison to SCP composite ($\Phi_{c,I} = 2 \pm 0.03$ vol%, $\Phi_{c,P} = 0.89 \pm 0.16$ vol%), MP sample showed higher percolation threshold values ($\Phi_{c,I} = 3.26 \pm 0.48$ vol%, $\Phi_{c,P} = 2.32 \pm 0.53$ vol%). The filler size of SCP and MP composites is similar and no segregation of GNPs were found for both, therefore the difference in $\Phi_c$ was mainly resulted from the different GNPs stacking states. This is in consistent with the morphology analysis which showed obviously tight and less homogeneous GNPs clusters for MP sample. According to Equation (5), $\Phi_c$ is directly proportional to the thickness $t$ in a 3-D isotropic conductive system. Considering the stacking of GNPs as the increase of GNPs thickness, the rise of $\Phi_c$ for MP sample with respect to SCP sample could be explained from the view of the simulation. The level of increase in
Φ_{c,P} was higher than that in Φ_{c,I}, this implies that stacking of GNPs caused more destruction of the conductive pathways in perpendicular direction.

MP sample showed lower log $\sigma_I$ and log $\sigma_P$ than SCP sample in Figure 8. The differences between the two composites were greater before the insulator-to-conductor transition of MP sample. However, as the volume fraction of GNPs increased above both percolation thresholds, the lower log $\sigma_I$ and log $\sigma_P$ of MP sample became closer and closer to those of SCP sample. From these findings, it can be concluded that the GNPs stacking had less impact on electrical conductivity than on percolation threshold.

### 3.7 Contribution of GNPs orientation to the anisotropic electrical properties

It can be seen from Figure 8 that the in-plane conductivity was about one or two orders of magnitude higher than the perpendicular direction for the same composites, which is consistent with the result of preferential in-plane orientation of GNPs stacks showing in SEM images. The percolation regions of in-plane direction where a steep increase in conductivity was observed were almost at higher filler loadings.

In order to quantitatively investigate the anisotropic electrical behaviors, the resulted $\Phi_c$ from Equation (4) is shown in Figure 9(a). Opposite to the result in other researches, $\Phi_{c,I} > \Phi_{c,P}$ was found in this work for SC, SCP and MP sample as shown in Figure 9(a). It might be ascribed to the significant difference in the geometry of GNPs and the conductivity measuring distance. It was found for a PMMA composite filled with carbon fiber having a large aspect ratio that the $\Phi_{c,I}$ and $\Phi_{c,P}$ were 1.80 ± 0.40 vol% and 0.27 ± 0.06 vol%, respectively. Although the in-plane orientation for GNPs was favorable during processing, it was much more difficult to form a continuous conductive network in a 25 mm-long in-plane measuring distance than in a 0.2 mm perpendicular measuring distance, with a mean diameter of GNPs between 25 and 40 μm. Unlike other samples, MSC sample had a higher $\Phi_{c,P}$ than $\Phi_{c,I}$. This could be attributed to the layered structure. The upper matrix-rich layer hindered the formation of connectivity network through the thickness, while the under GNPs-rich layer facilitated the connection along the in-plane direction.

In addition, anisotropy of the electrical conductivity was defined to be the ratio of experimental in-plane conductivity to perpendicular conductivity.

$$\text{Anisotropy} = \frac{\sigma_I}{\sigma_P},$$

The result is shown in Figure 9(b). The anisotropy of SC, SCP and MP sample increased with the GNPs fraction increasing as also found in other studies, relating to the faster increase rate of $\sigma_I$ than $\sigma_P$. This was caused by the increase in orientation level with GNPs fraction. However, the anisotropy of MSC sample decreased, since the layered structure became less with the filler content increasing. The result is in agreement with the morphology investigation in Figure 6.

---

**Figure 9** (a) Percolation threshold and (b) anisotropy in conductivity at different graphene nanoplatelets (GNPs) volume fraction for different samples [Color figure can be viewed at wileyonlinelibrary.com]
4 | CONCLUSIONS

In this work, four processing methods named SC, SCP, MSC, MP were used to fabricate PMMA/GNPs conductive composite films. The morphologies, both in-plane and perpendicular direction conductivities $\sigma$ and percolation threshold $\Phi_p$ of all the composites were investigated. The corresponding percolation thresholds of the composites varied from $0.42 \pm 0.13$ vol% to $3.26 \pm 0.48$ vol% and the conductivities varied up to two orders of magnitude. Among the four routes, the ability of improving electrical properties decreases in the sequence of SC $>$ MSC $>$ SCP $>$ MP. The contribution of GNPs size, distribution state (GNPs segregation and layered structure), dispersion state of fillers (stacking) and GNPs orientation to the electrical behavior of composites were revealed individually. Furthermore, the results were discussed and compared with other experimental studies and simulations. This work provide a deeper insight into understanding the individual effect of each factor and a systematic guide for the preparation of graphene-based polymer composite with superior electrical performances. Continuous research would further avoid the stacking by hybridizing GNPs with other fillers.

ACKNOWLEDGMENT

Open Access funding enabled and organized by Projekt DEAL. WOA Institution: FRIEDRICH-ALEXANDER-UNIVERSITAET ERLANGEN-NURNBERG. Blended DEAL: Projekt DEAL.

ORCID

Xiaoling Luo © https://orcid.org/0000-0001-6247-2343

REFERENCES

[1] J. Chen, B. Liu, X. Gao, D. Xu, RSC Adv. 2018, 8, 28048.
[2] T. A. Silva, F. C. Moraes, B. C. Janegitz, O. Fatibello-Filho, J. Nanomater. 2017, 2017, 4571614. https://doi.org/10.1155/2017/4571614.
[3] R. Socher, B. Krause, M. T. Müller, R. Boldt, P. Pötschke, Polymer 2012, 53, 495.
[4] I. Suarez-Martinez, N. Grobert, C. Ewels, Carbon 2011, 50, 741.
[5] X. Liu, W. Wu, B. Guo, M. Cui, H. Ma, Z. Zhang, R. Zhang, J. Mater. Chem. C 2021, 9, 214.
[6] M. Cao, D. Xiong, L. Yang, S. Li, Y. Xie, Q. Guo, Z. Li, H. Adams, J. Gu, T. Fan, Adv. Funct. Mater. 2019, 29, 1806792.
[7] A. Verma, A. Parashar, M. Packirisamy, Wiley Interdiscip. Rev. Comput. Mol. Sci. 2018, 8, e1346. https://doi.org/10.1002/wcms.1346.
[8] A. Verma, A. Parashar, Phys. Chem. Chem. Phys. 2017, 19, 16023.
[9] R. Ye, J. M. Tour, ACS Nano 2019, 13, 10872.
[10] A. Verma, A. Parashar, Mater. Res. Express 2018, 5, 115605.
[11] C. Teng, D. Xie, J. Wang, Z. Yang, G. Ren, Y. Zhu, Adv. Funct. Mater. 2017, 27, 1700240.
[12] A. Verma, R. Kumar, A. Parashar, Phys. Chem. Chem. Phys. 2019, 21, 6229.
[13] A. Verma, A. Parashar, M. Packirisamy, J. Appl. Phys. 2018, 124, 015102. https://doi.org/10.1063/1.5033542.
[14] W. Yu, L. Sisi, Y. Haiyan, L. Jie, RSC Adv. 2020, 10, 15328.
[15] A. Verma, A. Parashar, Diamond Relat. Mater. 2018, 88, 193.
[16] A. Verma, A. Parashar, M. Packirisamy, Mater. Today Proc. 2019, 11, 920.
[17] A. Verma, A. Parashar, Comput. Mater. Sci. 2018, 143, 15.
[18] A. Verma, A. Parashar, Nanotechnology 2018, 29, 115706.
[19] R. Tarcan, O. Todor-Boer, I. Petrovai, C. Leordean, S. Astilean, I. Botiz, J. Mater. Chem. C 2020, 8, 1198.
[20] D. Konios, M. M. Stylianakis, E. Stratakis, E. Kymakis, J. Colloid Interface Sci. 2014, 430, 108.
[21] R. Al-Gaashani, A. Najjar, Y. Zakaria, S. Mansour, M. A. Atieh, Ceram. Int. 2019, 45, 14439.
[22] K. Jiang, S. Siahrostami, T. Zheng, Y. Hu, S. Hwang, E. Stavitski, Y. Peng, J. Dynes, M. Gangisettey, D. Su, Energy Environ. Sci. 2018, 11, 893.
[23] H. Wang, C. Zhang, Z. Liu, L. Wang, P. Han, H. Xu, K. Zhang, S. Dong, J. Yao, G. Cui, J. Mater. Chem. 2011, 21, 5430.
[24] C. Ramirez, M. I. Osendii, J. Eur. Ceram. Soc. 2013, 33, 471.
[25] A. L. Margolin, T. V. Monakhova, P. M. Nedorezova, A. N. Klyaminuka, S. V. Polschikov, Polym. Degrad. Stab. 2018, 156, 59.
[26] A. J. Marsden, D. G. Papageorgiou, C. Vallés, A. Liscio, V. Palermo, M. A. Bissett, R. J. Young, I. A. Kinloch, 2D Mater. 2018, 5, 32003.
[27] H. Wu, L. T. D. Brian Rook, Polym. Compos. 2013, 37, 1.
[28] H. Wu, L. T. Drzal, J. Appl. Polym. Sci. 2013, 130, 4081.
[29] N. Yousefi, X. Lin, Q. Zheng, X. Shen, J. R. Potthins, J. Jia, E. Zussman, J. K. Kim, Carbon. 2013, 59, 406.
[30] X. Luo, M. Qu, D. W. Schubert, Polym. Compos. 2020, 42, 548.
[31] Z. Wang, X. Shen, N. M. Han, X. Liu, Y. Wu, W. Ye, J. K. Kim, Chem. Mater. 2016, 28, 6731.
[32] Z. Wang, X. Shen, M. Akbari Garakani, X. Lin, Y. Wu, X. Liu, X. Sun, J. K. Kim, ACS Appl. Mater. Interfaces 2015, 7, 5538.
[33] W. Gao, N. Zhao, T. Yu, J. Xi, A. Mao, M. Yuan, H. Bai, C. Gao, Carbon. 2020, 157, 570.
[34] S. Wu, R. B. Ladani, J. Zhang, E. Bafekrpour, K. Ghorbani, A. P. Mouritz, A. J. Kinloch, C. H. Wang, Carbon. 2015, 94, 607.
[35] M. Yoonessi, J. R. Gaier, J. A. Peck, M. A. Meador, Carbon. 2015, 84, 375.
[36] M. Santhosh, J. H. Choi, J. W. Choi, Nanomaterials 2019, 9, 1293. https://doi.org/10.3390/nano901293.
[37] H. Le Ferrand, S. Bolisetty, A. F. Demirörs, R. Libanori, A. R. Studart, R. Mezzenga, Nat. Commun. 2016, 7, 12078. https://doi.org/10.1038/ncomms12078.
[38] J. George, H. Ishida, Prog. Polym. Sci. 2018, 86, 1.
[39] S. Kormakov, D. Wu, J. Sun, X. Gao, X. He, X. Zheng, I. Skopincev, N. Memetov, A. Tkachev, Z. Zhi, Express Polym. Lett. 2019, 13, 713.
[40] A. A. Vasileiou, A. Docoslis, M. Kontopoulou, P. Xiang, Z. Ye, Polymer 2013, 54, 5230.
[41] V. Mittal, Macromol. Mater. Eng. 2014, 299, 906.
...Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Luo X, Schubert DW. Examining the contribution of factors affecting the electrical behavior of poly(methyl methacrylate)/graphene nanoplatelets composites. J Appl Polym Sci. 2021;138:e50694. https://doi.org/10.1002/app.50694