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The Effect of Agglomeration on the Electrical Percolation of Polyimide/Graphene Nanocomposites

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Abstract- Electrically conductive polymer/graphene nanocomposites are multipurpose in nature and have a wide range of potential applications in electronics and electrical engineering. The conductivity of these composites depends on a range of parameters such as the choice of polymer matrix, graphene filler type, the processing methodology and the quality of dispersion. The optimization of the dispersion process of graphene in the polymer matrix is a major challenge in the development of nanocomposites and their integration into industrial applications. This paper investigates the efficacy of centrifugation as a means of isolating smaller graphene agglomerates from the supernatant after initially dispersing the material in polyamic acid using high shear mixing. The relationship between the centrifugation time and agglomerate size and its effect on the electrical percolation of the polymer nanocomposite is elucidated. A set of polyimide films prepared using varying centrifugation times and graphene nanoflake concentrations were prepared by thermal imidization and electrically characterized to assess the impact of the structure of the nanocomposite on the electrical percolation threshold. Graphene nanoflakes agglomerates were reduced in size by increasing the centrifugation time and this led to a decrease in the electrical conductivity of the final films. The electrical conductivity of polyimide graphene (PI/G) nanocomposites consistently increased with increasing filler concentration. PI/G prepared using 2 min centrifugation times exhibited an electrical conductivity of 2.7×10^{-3} S/m, while the corresponding PI/G prepared using 5 min of centrifugation had an electrical conductivity of 0.16×10^{-3} S/m. The percolation phenomena were clearly observed for all nanocomposites as the conductivity rose from $\sim 10^{-13}$ to $\sim 10^{-3}$ S/m, while the percolation thresholds varied depending on the centrifugation time (agglomeration density).

I. INTRODUCTION

The superior electrical conductivity of graphene nanocomposites has attracted a lot of attention and paved the way for future integration into industrial applications. Graphene-based polymer nanocomposites prepared by incorporating graphene into different host matrices, various polymers, and epoxy matrices [1-2] have been used to enhance electrical conductivity. As a function of filler content, the electrical conductivity of nanocomposites shows a nonlinear behavior [3]. The electrical conductivity and percolation threshold of nanocomposites are both related to the filler content and the dispersion process. Dispersion of the fillers within the organic matrix is a critical step in polymer nanocomposite preparation. A well-dispersed state ensures a maximized contact

interface between the polymer chains and the graphene, which will affect the overall performance of the nanocomposites [4]. For nanocomposite development in industrial applications, optimizing the graphene dispersion process in a polymer matrix is a major challenge, as removing agglomeration allows optimal exposure of the graphene surface to the polymer matrix. Many efforts have been made to enhance the graphene dispersion in polymer matrices such as chemical functionalization [5], and the use of different dispersion equipment such as sonication probes, planetary mixing, and high shear mixing [6]. However, it is still difficult to prepare a uniform morphology with a fine dispersion of interconnected graphene derivatives due to their inherent affinity to agglomerate. The morphology of the conductive network (graphene nanoflakes) and dispersion quality have a major influence on the final electrical conductivity of polymer nanocomposites. The agglomerated structures can affect the electrical properties of nanocomposites and lead to percolation at lower filler concentrations [7], called selective localization. In the present paper, the effect of centrifugation time on the dispersion quality (reducing agglomeration, particle distribution, aggregate size) is reported. Such an effect of the graphene concentration is then correlated with the electrical conduction of PI/G nanocomposites for a given centrifugation parameter.

II. EXPERIMENTAL PART

A. Materials

The polyimide host matrix used in this study is synthesized from a polyamic acid (PAA) precursor solution consisting of pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) in an N-Methyl-2-pyrrolidone (NMP) solvent. The final polyimide has a density of 1.1 g/cm^3 . The graphene nanoflakes have been commercially sourced.

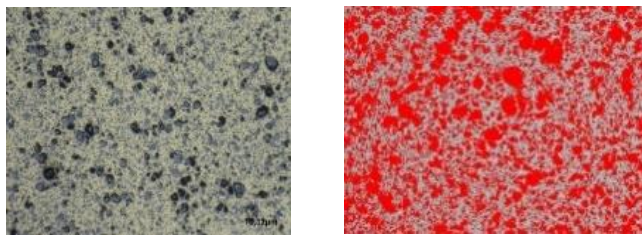
B. Preparation of PI/Graphene nanocomposites

The as-purchased graphene nanoflakes were added to the PAA solution and subsequently mixed at room temperature using a high shear mixer. A centrifugation step (14 800 rpm) was then performed to reduce the agglomerate size and density. The supernatant graphene/PAA mixture was spin-coated onto silicon wafer substrates. The spin speed was adjusted to yield PI/G nanocomposite films with a thickness of approximately 10

μm after curing at high temperature in a controlled oven under a nitrogen atmosphere. The nanocomposite layers were then peeled off from the substrates by wet stripping.

C. Characterization

The graphene nanoflakes within the PI layer were macroscopically evaluated using a digital microscope, where a series of top-down images were acquired in multiple areas. The agglomerates and the detectable dispersed graphene flakes sizes were calculated and counted by using combined surface mapping with Gwyddion numerical image treatment software. Fig. 1 shows an example of numerical image treatment analysis where the particles and agglomerates are marked by a threshold to count and rank them by size.



(a) (b)

Fig. 1. Optical microscope top view image (a) and after numerical treatment analysis (b).

Electrical conduction was assessed by using broadband dielectric relaxation spectroscopy (BDRS) in a large frequency range from 10^{-1} to 10^6 Hz. The AC conductivity (σ_{AC}) of PI/G nanocomposites was measured at room temperature for various processing parameters, in particular centrifugation time and graphene content.

III. RESULTS AND DISCUSSION

A. Effect of centrifugation time on reducing agglomeration size

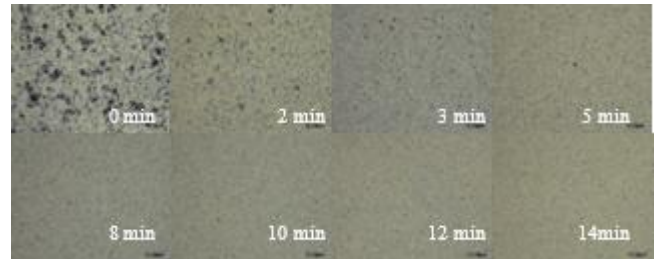
The presence of large graphene agglomerates in the final films can lead to percolation at low graphene concentrations. Consequently, it is considered that the less agglomeration that occurs, the better the dispersion quality.

To study the effect of agglomeration density on the electrical conductivity, a set of PI/G nanocomposites was prepared with equal graphene filler content (0.5 wt.%) using high shear mixing. Subsequently, to remove large agglomerates, centrifugal decantation by microcentrifugation was used to reduce the agglomerate size and density. To achieve this, PAA/G solutions were placed in 3 ml tubes before being subjected to a centrifugal force of 21 000 G (14 800 rpm) for various times. The supernatant was then recovered and used to prepare the PI/G nanocomposite.

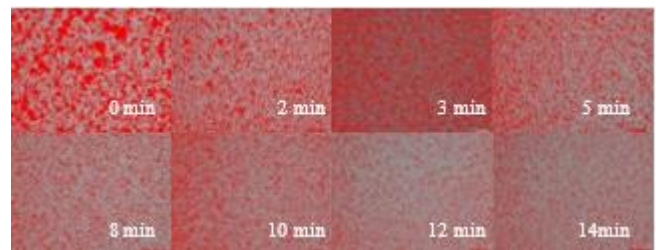
Numerical analysis (see Fig. 2) shows the graphene flakes and the agglomeration size distribution for PI/G nanocomposites with different centrifugation times ranging from 0 to 14 min. One can clearly see the decrease in the graphene agglomerate size in the PI/G nanocomposite films prepared with increasing centrifugation time. The dispersion homogeneity is enhanced due to the decrease in residual agglomeration. Fig. 3 shows the

nanoflakes size distribution in the PI films for various centrifugation times for the same initial graphene concentration (0.5 wt.%). The number of detected graphene particles (down to 400 nm as a minimum in the lateral dimension of the layer) remains stable with increasing centrifugation time.

Meanwhile, the maximum agglomerate size detected in the PI/G nanocomposite films decreases from approx. 90 μm without centrifugation down to approximately 10 μm after 14 min.



(a)



(b)

Fig. 2. Graphene flakes dispersion and agglomeration size reduction in PI/G nanocomposite films (0.5 wt.%) with different centrifugation times from 0 to 14 min: top view image (a) and after numerical treatment analysis (b).

These changes in the agglomerate size can affect the electrical conduction as the electrical conductivity decreases with decreasing particle size [8].

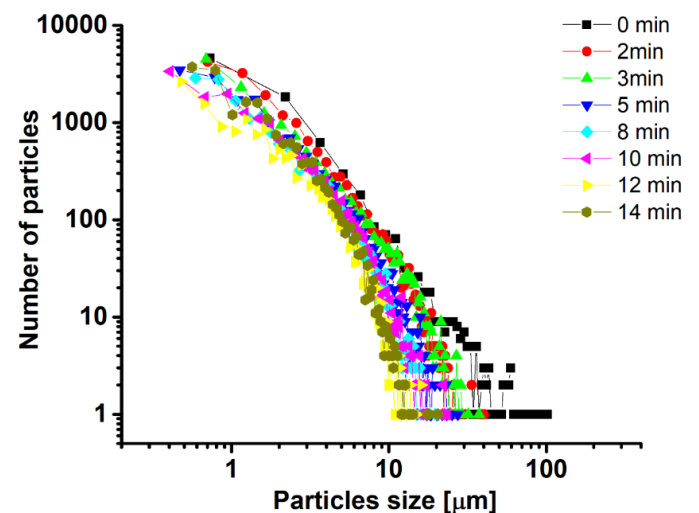


Fig. 3. Particles size distribution for different centrifugation times.

B. Effect of centrifugation time on electrical conductivity

To investigate the impact of graphene agglomeration on the electrical conduction of the PI/G nanocomposite, AC conductivity measurements were carried out on the PI/G nanocomposite films prepared with centrifugation times from 0 to 14 min. Fig. 4 presents the frequency-dependency of the AC conductivity of PI/G nanocomposites with 0.5 wt.% graphene content for each centrifugation times. Contrary to the pure PI film that exhibits an expected power-law behavior of the AC conductivity versus frequency (slope $n=1$) typical of a highly insulating material [9], PI/G nanocomposite films with centrifugation times going from 0 to 10 min show a more or less predominant DC conductivity component, occurring through a horizontal frequency-independent conductivity plateau. That is a more resistive material feature rather than capacitive [10].

Moreover, a higher graphene agglomeration results in a higher DC conductivity. This indicates that the carrier mobility and/or density in the PI/G nanocomposite films is higher and dependent on the graphene agglomeration and concentration and that charges can move more quickly, likely within the graphene layers, throughout the nanocomposites. However, PI/G nanocomposite films with 10, 12 and 14 min of centrifugation exhibit a similar behavior compared to the neat PI. This could be explained by the fact that there is less agglomeration in these films and the charge could not move throughout the nanocomposites by a direct particle-to-particle percolation.

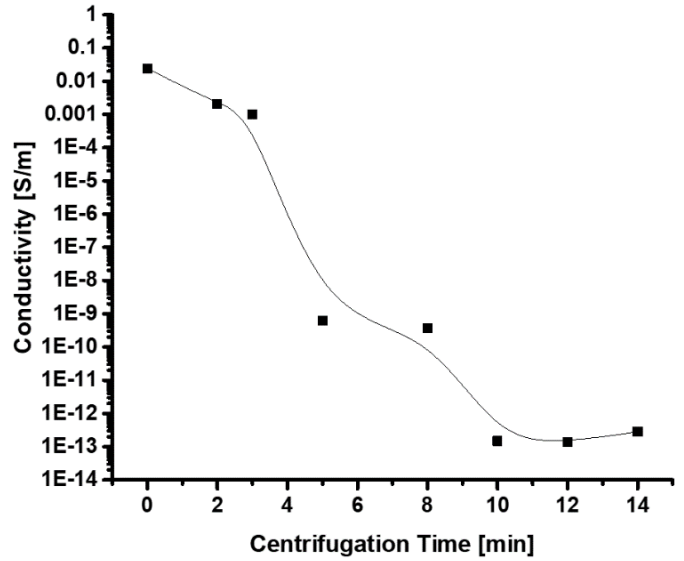


Fig. 5. DC conductivity of PI/G nanocomposites as a function of centrifugation time.

C. Effect of Graphene Concentration on the Electrical Properties of PI/G Nanocomposites

To investigate the impact of graphene agglomeration on the electrical conduction of the PI/G nanocomposite and to determine the electrical percolation threshold of the material, a series of samples were prepared with varying graphene filler concentrations. Based on the results from Sections A and B, graphene nanoflakes were prepared using two centrifugation times: 2 min (PI/G2) and 5 min (PI/G5). AC conductivity measurements were carried out on these PI/G nanocomposite films with different graphene concentrations (0 to 2 wt.%). The electrical conductivity of PI/G composites consistently increases with increasing filler concentration, as shown in Fig. 6. The PI/G2 exhibited an electrical conductivity of 2.7×10^{-3} S/m, whilst the corresponding PI/G5 has an electrical conductivity of 0.16×10^{-3} S/m.

The percolation phenomena were observed for all the composites as the conductivity rose from $\sim 10^{-13}$ to $\sim 10^{-3}$ S/m whilst the percolation thresholds were different depending on the centrifugation time (agglomeration density). The percolation threshold of the nanocomposites made from PAA/graphene with 2 min was 0.06 wt.%, whereas the film with 5 min centrifugation time exhibited a percolation threshold at 0.8 wt.%. The percolation threshold at such a low concentration for samples with 2 min centrifugation times could be explained by the fact that the graphene agglomerate sizes increase with increasing filler concentration [11].

As shown in Fig 7, PI/G2 film exhibits large agglomerate compared to the PI/G5. The maximum agglomerate size decreases from 45 μm for PI/G prepared with 2 min of centrifugation to 24 μm with 5 min of centrifugation.

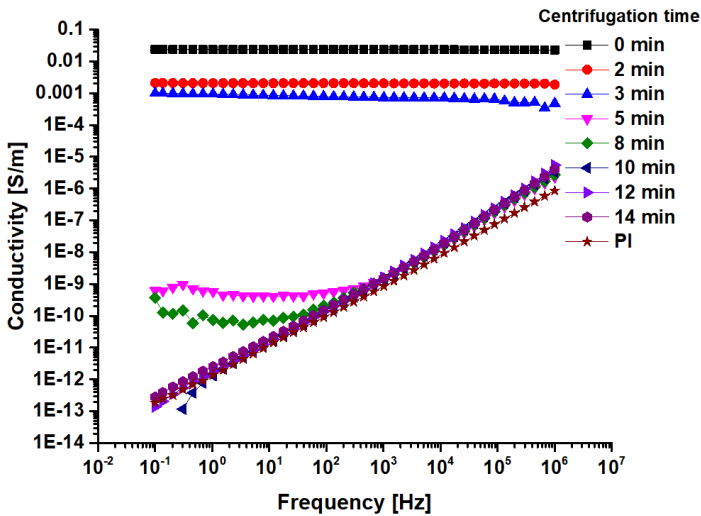


Fig. 4. AC conductivity of PI/G nanocomposites versus frequency for different centrifugation times.

The electrical conductivity σ_{DC} (data extracted from Fig. 4 at 10^{-1} Hz) of the PI/G nanocomposite films as a function of graphene centrifugation time is shown in Fig. 5. It can be observed that σ_{DC} of the PI/G films decreases from 10^{-3} S/m (percolated film) to 10^{-13} S/m with decreasing graphene agglomeration (i.e. increasing centrifugation time). The effect of agglomeration on percolation was observed as the conductivity decreased from 10^{-3} to 10^{-13} S/m with increasing centrifugation time.

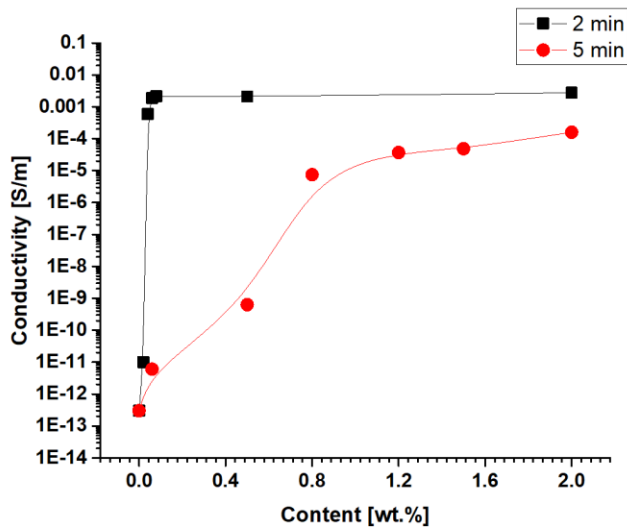


Fig. 6. DC conductivity of PI/G nanocomposites as a function of graphene content after 2 min and 5 min centrifugation time.

The larger nanoflakes are more likely to form an interconnected 3D network at a lower filler content due to the higher aspect ratios compared to smaller nanoflakes. A large difference in percolation threshold is expected because the graphene sheets have an intrinsic ability to form an interconnected 3D network at a lower filler concentration due to their high aspect ratios than the smaller G sheets.

The comparison of percolation thresholds clearly indicates that the density and agglomerate size have an important role in graphene percolation.

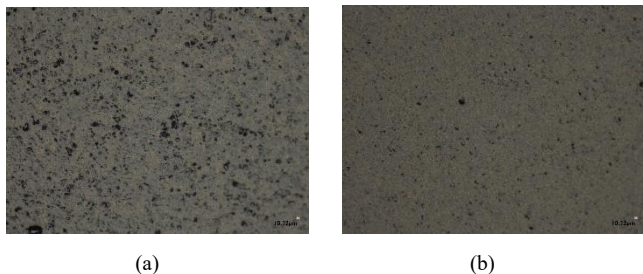


Fig. 7. Optical microscope top view image with 2 wt.% graphene content: (a) PI/G2 and (b) PI/G5.

IV. CONCLUSION

The relationship between graphene percolation and the effect of agglomerate size and density on the electrical conductivity of polyimide nanocomposite films was reported in this paper. The results show an improvement in dispersion quality (reduced agglomerate size and density) with increasing centrifugation time. PI/G nanocomposites prepared with a centrifugation step present less agglomeration compared to the samples without, which affects the final electrical properties of the nanocomposites. Based on these results, a set of PI/G nanocomposites with a range of graphene concentrations were prepared with 2 min and 5 min of centrifugation to study the electrical conduction and percolation threshold of the material.

The electrical conductivity of PI/G composites consistently increases with increasing filler content. The PI/G with 2 min centrifugation times exhibited an electrical conductivity of 2.7×10^{-3} S/m, whilst the corresponding PI/G with 5 min centrifugation has an electrical conductivity of 0.16×10^{-3} S/m. The percolation threshold of PI/G with 2 min of centrifugation was 0.06 wt.% compared to 0.8 wt.% for PI/G with 5 min of centrifugation. This large difference in the percolation threshold is expected as the maximum agglomerate size decreases from 45 μm for PI/G prepared with 2 min of centrifugation to 24 μm with 5 min of centrifugation. The centrifugation step seems to be crucial to control the electrical conductivity of the nanocomposites and has a progressive effect on conductivity mitigation.

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