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The Effect of Graphene Dispersion on the Electrical Properties of Polyimide Nanocomposites

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Abstract- Graphene-based polymer nanocomposites have attracted widespread industrial interest as the electrical conductivity of the material can be precisely controlled due to the unique conduction properties of graphene. In this paper, we show the effect of exfoliation methods and dispersion time on the particle dispersion, aggregate size and the overall electrical conduction of polyimide/graphene nanocomposites. A set of polyimide films with a varying graphene nanoflake content were prepared by thermal imidization and electrically characterised to assess the impact of the composition of the nanocomposite on the electrical percolation threshold. Three dispersion techniques were investigated (i.e. high shear mixing, ultrasonication probe and planetary mixing) and it was found that the size of the graphene nanoflakes was reduced by increasing the dispersion time in each case. The highest dispersion quality was obtained using the high shear mixing technique which yielded an electrical percolation threshold of 0.03 wt%.

I. INTRODUCTION

Polyimide (PI) is a high-performance polymer used in a variety of industries [1]. However, the low electrical conductivity limits some of the applications of PI in aerospace and electronics applications [2]. In particular, the control of the electrical properties is a key issue for applications such as stress grading [3,4] and electromagnetic shielding [5]. Many efforts have been made to control PI electrical conduction by incorporating conductive particles in the matrix and varying the filler content below or beyond the percolation threshold. Previously, carbon nanofibers (CNF) [6], carbon nanotubes (CNT) [7] or graphene layers [8] have been used for that purpose. Among these materials, graphene is the most attractive due to its excellent electrical conductivity.

The morphology of the conductive network (graphene nanoflakes) and dispersion quality have a major influence on the electrical conductivity of polymer nanocomposites. It is known that the electrical percolation threshold of polyimide/graphene (PI/G) nanocomposites is around 0.5 wt.% [9-10]. To reduce the amount of graphene required, the percolation threshold of the PI/G nanocomposite should be minimized. This can be adjusted by controlling the dispersion quality of the conductive network in the polyimide matrix via different methods, such as shear mixing [11-12] or sonication [13-14].

In this paper, we show the effect exfoliation methods (high shear mixing, ultrasonication and planetary mixing) have on the dispersion quality and aggregate size of graphene within the PI matrix. The impact of the graphene content on the electrical conduction of PI/G nanocomposites is also assessed.

II. EXPERIMENTAL

A. Materials

The polyimide host matrix used in this study is synthesized from polyamic acid (PAA) precursor solution consisting of pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) in a N-Methyl-2-pyrrolidone (NMP) solvent. The final polyimide has a density of 1.1 g/cm³. Fig. 1 shows the PI monomer used in this study.

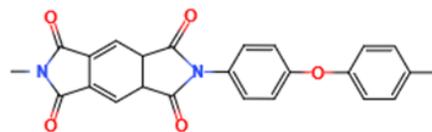


Fig. 1. Chemical structure of PMDA/ODA polyimide.

Graphene nanoflakes have been commercially sourced. Fig. 2 depicts TEM images of the obtained nanolayers before mixing in PAA solution.

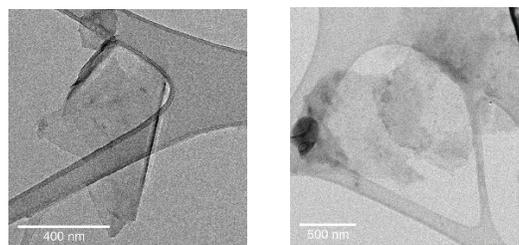


Fig. 2. TEM images of graphene nanoflakes.

B. Preparation of PI/Graphene nanocomposites

The as-purchased graphene nanoflakes were added to the PAA solution and subsequently mixed at room temperature using three different exfoliation methods: i. high shear mixer (5000

rpm), ii. Ultrasonication (300W with a square wave 2s on and 10 s off) and iii. planetary mixer (1800 rpm).

The resulting graphene/PAA mixture was spin-coated onto silicon wafer substrates. The spin speed was adjusted to yield PI/G nanocomposite films with thickness of approx. 14 μm after curing at high temperature in a controlled oven under nitrogen atmosphere. The nanocomposite layers were then peeled off from the substrates by wet stripping. Fig. 3 presents a general chart of the process steps for PI/G nanocomposites elaboration.

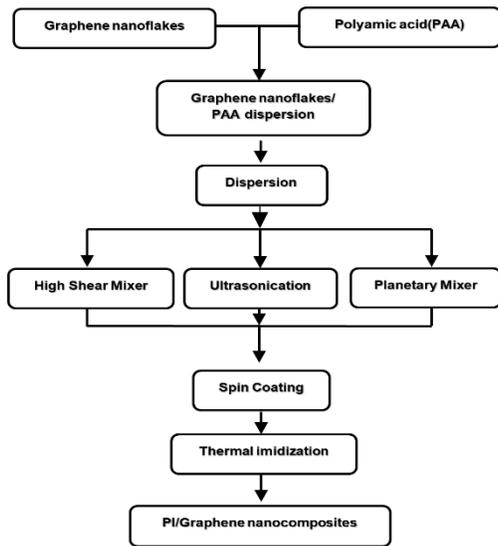


Fig. 3. Elaboration process chart of PI/G nanocomposites.

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 aggregates and the detectable dispersed graphene flakes sizes were counted by using combined surface mapping with the Gwyddion numerical image treatment software. Fig. 4 shows an example of numerical image treatment analysis where the particles and aggregates are marked by a threshold to count and rank them by size.

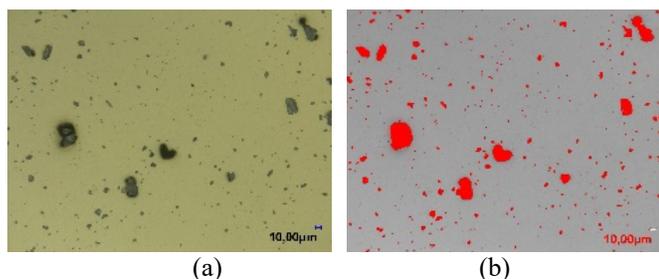


Fig. 4. Optical microscope top view image (a) and after numerical treatment analysis (b).

Electrical conduction was assessed by using broadband dielectric relaxation spectroscopy (BDRS) in a large AC

frequency range from 10^{-1} to 10^4 Hz. The AC conductivity (σ_{AC}) of PI/G nanocomposites was measured at room temperature for various processing parameters, in particular dispersion methods and time.

III. RESULTS AND DISCUSSION

A. Effect of dispersion methods on particles and agglomeration sizes.

The dispersion quality has a crucial effect on the final nanocomposite properties. The less aggregation the better the dispersion quality. Mainly, two parameters may affect the dispersion quality: the exfoliation technique used to process the material and the exfoliation time.

To study the effect of the exfoliation method on the dispersion quality, three PI/G nanocomposites were prepared with equal graphene filler content using either high shear mixing, ultrasonication probe or planetary mixing as the dispersion technique. The dispersion time was constant for each sample. Numerical analysis (Fig. 5) shows the graphene flakes and the aggregation size distribution for PI/G nanocomposites (with 0.05 wt.% of content) dispersed for 2 h with the three different techniques. The film dispersed with the planetary mixer shows the poorest exfoliation and aggregate size reduction, whereas the high shear mixer exhibits the most efficient dispersion with less large aggregates and more dispersed flakes within PI. Moreover, it was observed that high shear mixing inhibits the re-agglomeration of graphene post-dispersion in the PAA solution (better particle stability) compared to the other techniques (not shown here).

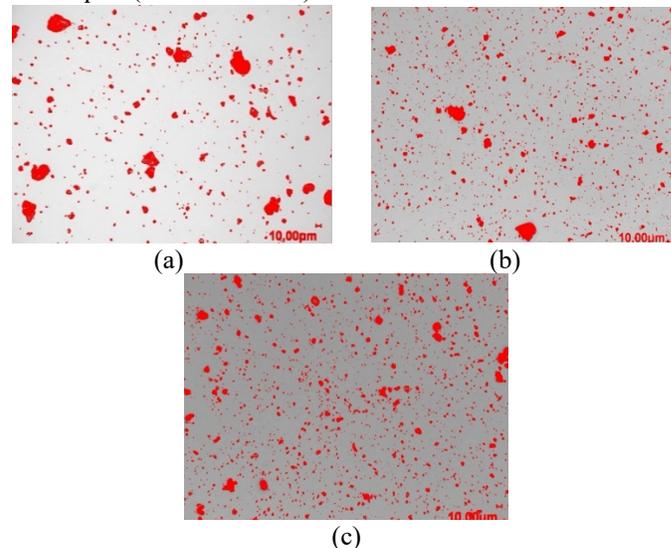


Fig. 5. Graphene flakes and agglomeration size in PI/G nanocomposite films (0.05 wt.%) after 2 h of dispersion by planetary mixing (a), sonication (b) and high shear mixing (c).

B. Effect of time on particle dispersion and agglomeration size reduction

To study the effect of mixing time, three nanocomposites with the same filler content was prepared using dispersion times in the PAA of 15 min, 2 h and 5 h. The high shear mixer was used

to disperse the graphene in each case as this is the most effective dispersion method compared to ultrasonication and planetary mixing (Fig. 5).

Fig. 6 shows the dispersion of graphene flakes and agglomeration size reduction in PI/G nanocomposite films (0.05 wt%) obtained by high shear mixing for dispersion times of 15 min, 1 h and 5 h. One can clearly observe the progressive improvement in the dispersion of graphene flakes with increasing dispersion time, with the smallest aggregate size achieved after 5 h.

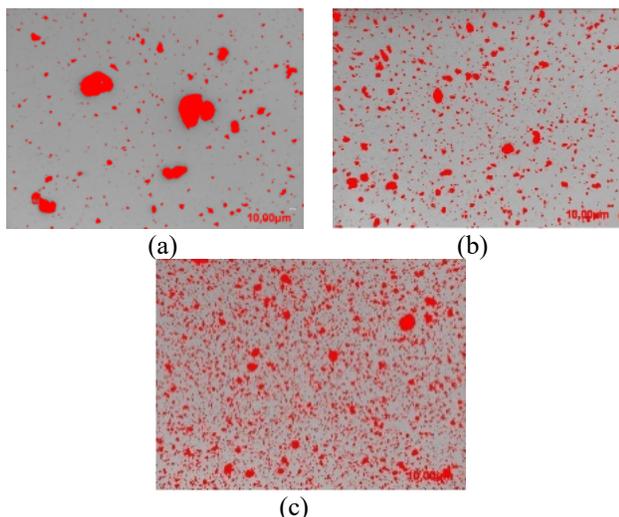


Fig. 6. Graphene flakes dispersion and agglomeration size reduction in PI/G nanocomposite films (0.05 wt%) dispersed for 15 min (a), 1 h (b) and 5 h (c) by high shear mixing.

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

To investigate the impact of graphene concentration 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 content. Based on the results from Section A and B, the graphene nanoflakes were dispersed in the PI matrix by means of high shear mixing for 5 h, given this is the most effective dispersion procedure of those under investigation.

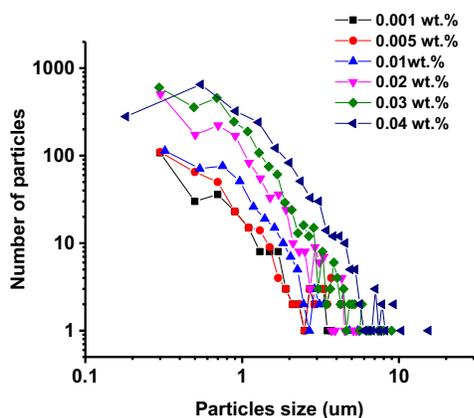


Fig. 7. Particles size distribution for different graphene nanoflakes contents.

Fig. 7 shows the nanoflakes size distribution for various graphene concentrations dispersed in the PI film ranging from 0.001 wt.% up to 0.04 wt.%.

The number of detected graphene particles (down to 300 nm as a minimum in the lateral dimension of the layer) for a given aggregate size increases with increasing graphene content. Meanwhile, the maximum aggregate size detected in the PI/G nanocomposite films is also increased from 2 μm at low content (0.005 wt.%) up to approx. 10 μm at 0.04 wt.%. This is an important parameter with respect to the electrical conduction of the nanocomposite, with previous studies showing an increase in electrical conductivity with increasing particle size [15].

To study the effect of the graphene content on the electrical properties, AC conductivity measurements were carried out on the PI/G nanocomposite films with the different graphene concentrations.

Fig. 8 presents the frequency-dependency of the AC conductivity of PI/G nanocomposites for different graphene concentrations from neat PI up to 0.04 wt.%. 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 high insulating material [16], all the PI/G nanocomposite films show a more or less predominant DC conductivity component, occurring through a horizontal frequency-independent conductivity plateau. That is a feature of a more resistive material rather than capacitive [17]. Moreover, higher graphene concentrations result 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 content and that charges can move more quickly, likely within the graphene layers, throughout the nanocomposites.

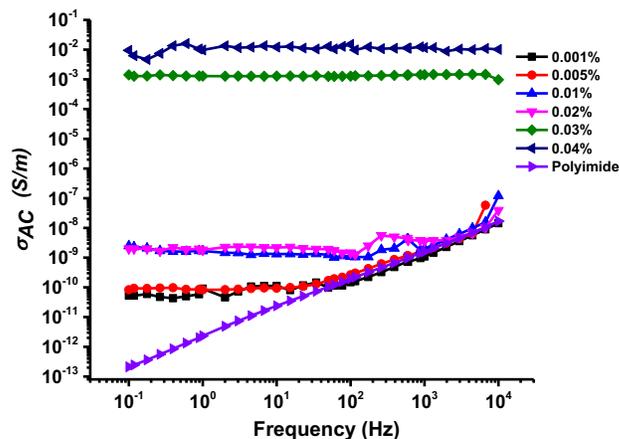


Fig. 8. AC conductivity of PI/G nanocomposites versus frequency for different graphene contents.

The electrical conductivity σ_{DC} (data extracted from Fig. 8 at 10^{-1} Hz) of the PI/G nanocomposite films as a function of graphene concentration is showed in Fig. 9. It can be observed that σ_{DC} of the PI/G films increases with increasing graphene concentration (from 10^{-13} to 10^{-8} S/m) up to 0.02 wt.%. The electrical percolation threshold was clearly observed as the

conductivity rises suddenly from 10^{-8} to 10^{-3} S/m when the graphene concentration reached 0.03 wt.%.

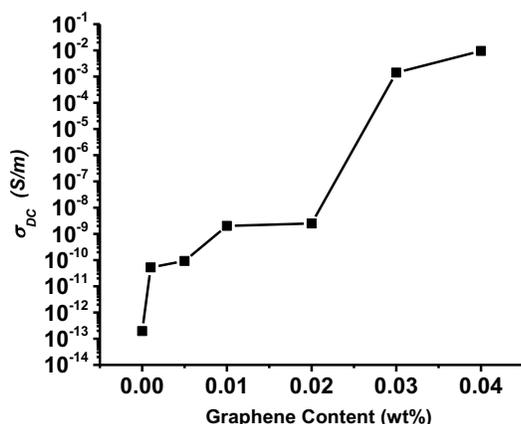


Fig. 9. DC conductivity of PI/G nanocomposites as a function of graphene content.

The percolation threshold at such a low content could be explained by the fact that the graphene aggregates sizes increase with increasing filler content as showed in Fig. 7. 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. The percolation threshold could be reduced by using chemically modified graphene to avoid aggregation at low content.

IV. CONCLUSION

The effect of graphene exfoliation procedures (methods and time) in a PI matrix on the electrical conductivity of nanocomposite films is reported. The results show an improvement of dispersion quality with increasing dispersion time. PI/G nanocomposites prepared by high shear mixing present less aggregation compared to nanocomposites prepared by sonication and planetary mixing. Based on this result, a set of PI/G nanocomposites with a range of graphene concentrations were prepared to study the electrical conduction and percolation threshold of the material. The AC conductivity exhibits a frequency-independent behavior when the graphene content is larger than 0.02 wt%. The percolation threshold for the PI/G nanocomposites is obtained for a low filler content of 0.03 wt%, with an electrical conductivity rising up to $>10^{-3}$ S/m.

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