Juniper Online
Journal Material Science
ISSN: 2575-856X

Research Article
Volume 8 Issue 4 - March 2024
DOI: 10.19080/JOJMS.2024.08.5557241

JOJ Material Sci

Dielectric and Mechanical Properties of Polyimide/3D Graphene Flexible Composite Films

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Submitted: March 04, 2024; **Published:** March 14, 2024

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Abstarct

Three-dimensional graphene (3D graphene) is a material composed of two-dimensional graphene with three-dimensional structure. It has attracted extensive attention from researchers because of its many excellent physical and chemical properties. The applications of polyimide/3D graphene films are widely studied, but there are few reports on polyimide/3D graphene composite films. Here, 3D graphene was prepared by chemical vapor deposition (CVD), and polyimide (PI)/graphene oxide and polyimide/3D graphene composite films were produced by the in-situ polymerization. The composite films were characterized by Raman scattering spectra, scanning electron microscopy (SEM), Fourier transform infra-red spectroscopy (FTIR), transmission electron microscopy (TEM) and Dielectric Spectrometer analyses. 3D graphene can be closely connected with PI matrix, with ultrahigh surface area and good compatibility on the incorporation 3D graphene polymer composites, which is more beneficial for functioning the electrical properties advantages of graphene and improving the dielectric properties of film. In the meanwhile, the uniform dispersion of the three-dimensional network structure in polymer matrix is of certain function in preventing graphene sheet stacking during the polymerization process. The doping of three-dimensional graphene not only increases the dielectric properties of polymer materials, but also improves the mechanical properties of composite materials. Those composite films are flexible and meet the basic requirements of flexible materials.

Keywords: Three-dimensional graphene; FTIR; Chemical vapor deposition; Dielectric Spectrometer analyse

Introduction

Polymer matrix composites have attracted great attention due to their unique properties, such as good flexibility, dielectric properties, machining properties, durability, sensitivity and thermal stability [1,2]. Polyimide (PI) is an aromatic heterocyclic polymer containing phthalate imine ring repeat unit. Due to its superior thermal, electrical and mechanical properties, PI is widely used in aviation, aerospace, nuclear power, microelectronics and other fields [3-5]. It is well known that the improvement in dielectric properties and corona resistance of these polymers is achieved by dispersing a certain number of inorganic nanoparticles into the polymer. And graphene is a single-atom thick two-dimensional carbon nanomaterial, with excellent optical, electrical, thermal and mechanical properties, and can significantly improve the mechanical, thermal and dielectric properties of polymer matrix composite materials [6,7]. As a new type of flexible, high-strength, light-weight and high-properties dielectric materials, polymer/graphene composite materials show a promising application prospect in many fields, including thin film capacitors, very large-scale integrated circuit and electrode materials [8,9]. Samsung released phones with foldable screens in 2018. With the ordinary “hard” smart phone, foldable mobile phone with flexible display touch screen, consumers can easily bend and twist. An analysis report points out that flexible display screens are currently mainly made of Polyimide (PI) instead of glass as a substrate, so that the screen becomes flexible, turning the hard screen into a soft screen. However, due to the insufficient surface-active groups of graphene, it is difficult to form a strong interaction between polymer interfaces directly, as well as it is difficult to achieve the intensified effect of graphene in polymer composite materials. In addition, there is a strong π-π interaction between graphene sheets, realizing the sheets a strong aggregation trend [10-12]. Therefore, 3D graphene exhibits the excellent properties of 2D graphene three-dimensionally graphene with a larger specific surface area, interconnected fibers, which can form a good network in polymer matrix, with excellent electrical and mechanical properties. The applications of polyimide/2D graphene films are widely studied, but there are few reports on polyimide/3D graphene composite films.

In this study, we applied the chemical vapor deposition to prepare three-dimensional graphene, and combined the in-situ polymerization to prepare polyimide/graphene oxide (GO) and polyimide/3D graphene composite film. During the preparation process of composite materials, three-dimensional graphene can be closely connected with PI matrix to form many "Micro electric Containers", which is more beneficial for functioning the electrical properties advantages of graphene and improving the dielectric properties of composite films. The dielectric and mechanical properties of graphene oxide/ polyimide and polyimide/3D graphene composite films were compared.

Experimental Section

Reagent

Oxidized graphite, diameter of 0.3-2.0 µm, the Sixth Element (Chang zhou) Materials Technology Co., Ltd.; Pyromelliticdianhydride (PMDA), Tianjin Chemical Reagent Factory Fu Chen Co., Ltd; 4, 4-Diaminodiphenyl ether (ODA); N, N-dimethylacetamide (DMAc), Tianjin Fuyu Chemical Reagent Co., Ltd.

Preparation of three-dimensional graphene

To cut the foamed nickel to size of 50 mm × 40 mm to function as the base material. To clean with deionized water, absolute ethanol and acetone in an ultrasonic cleaning machine for 5 min to put foamed nickel into the drying oven for drying after cleaning.

To put the foamed nickel into quartz boat, and to push the quartz boat into the middle of CVD (chemical vapor deposition) tubular furnace and the heating area of furnace; then, after placing the base material for preparing three-dimensional graphene, to tighten the flapper valves at both ends of CVD furnace. Keep the flow rate of Ar gas (500 mL/min) and H2 (30 mL/min) unchanged, and heat up to 1000 °C at a constant speed. After the preheating, ethanol (analytically pure, ambient temperature 15 °C) was put into the quartz tube with Ar gas (100 mL/min) and kept for 10-30 min. Then, it was cooled to room temperature to preparation of three-dimensional graphene.

Preparation of polyimide/graphene oxide composite film

Taking the composite film containing mass fraction of 1 % (all doping concentrations used in this article are by weight) GO as an example, to ultrasonically disperse the oxidized graphite in DMAc for 12 hours to obtain GO dispersion solution; to add GO dispersion solution into a flask equipped with nitrogen protection and mechanical stirring, and add ODA to this solution, DMAc were added in batches when PMDA and ODA were with a molar ratio of 1.06:1. And continuous stirring for 2 h, to form a uniform GO/PAA(polyamic acid) solution, then the mixture was casted on clean glass plates and dried in an air convection oven at 80°C for 5 h, and post-cured in air oven at 120, 200 and 300 °C for 2 h respectively. Finally, composite films containing 2 % GO and pure PI films are prepared by adopting similar in-situ polymerization as shown as figure 1, with the film thickness of about 80 μm.

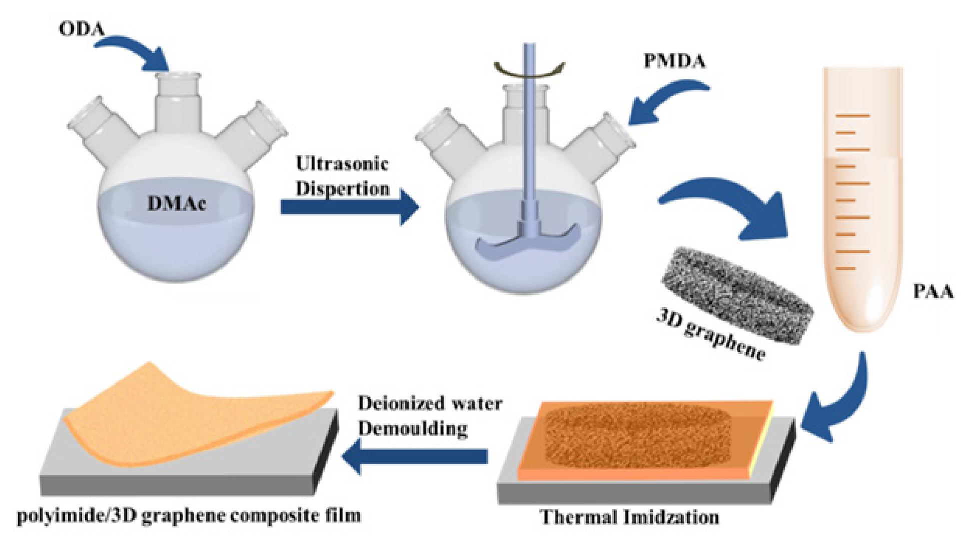

Figure 1: The processing of PI/3D graphene composite film.

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Preparation of Polyimide/3D Graphene Composite Film

To immerse the three-dimensional graphene sample prepared on foamed nickel in 0.5 mmol $FeCl_3$ solution to remove the nickel substrate; then, to add 3 g of ODA into a three neck flask, and to add 3.28 g of PMDA and 36ml of DMAc in batches to obtain a viscous PAA composite solution when PMDA and ODA were with a molar ratio of 1.06:1. Finally, to place the three-dimensional graphene without the nickel substrate on a glass sheet, to cover with PAA composite solution, and obtain polyimide/3D graphene composite film after imidization, the mass fraction of 3D graphene in PAA solution is about 2 %, with a thickness of about 80 μm.

Sample Characterization

Raman scattering measurements were carried out on a Renishaw RM1000 Raman microscope working at 532 nm wavelength of laser light, the scattered intensity is the average of 20–50 spectra recorded for an acquisition time of 10 s using a × 50 objective that formed scattering spots of ~10 mm diameter. Morphology of the samples was studied by scanning electron microscope (SEM, FEI Quanta 200) and transmission electron microscopy (TEM, JEM-2000FX). The FTIR spectra were recorded by Bruker EQUINOX55. Spectra were obtained with 200 scans at a resolution 2 cm^{-1}. The broadband dielectric spectroscopy was tested using a Novo control Dielectric Spectrometer (GmbH Germany), CONCEPT 40. Tensile tests experiments were conducted on an Instron Machine (Tinius Olsen H10K-S Benchtop Testing Machine). All of samples were cut to sheets with a width of 5 mm, the dimensions of mechanical test specimen were 100 mm × 3 mm × 0.06 mm.

Results and Discussion

The pictures of PAA, PI/GO-1 %, PI/GO-2 % and PI/3D graphene composite films are shown in figure 2. As can be seen from figure 2b, the higher the concentration of GO, the darker the color of the polyamic acid solution, and the polyamic acid solution is uniform without precipitation. PI/GO-1%, PI/GO-2% and PI/3D graphene composite films are flexible composite films, with excellent flexibility. Those composite films are flexible and meet the basic requirements of flexible materials. The SEM images of PI, 3D graphene and GO are shown in figure 3. As shown in figure 3a, the surface and sides of PI are flat and smooth, with high cleanliness of section, and no other nanomaterial mixing. As shown in figure 3c, the surface and sides of GO are flat, showing a typical layered morphology. As shown in figure 3b, the surface and sides of three-dimensional graphene are flat, showing a typical layered morphology, and interconnected three-dimensional frameworks at the same time.

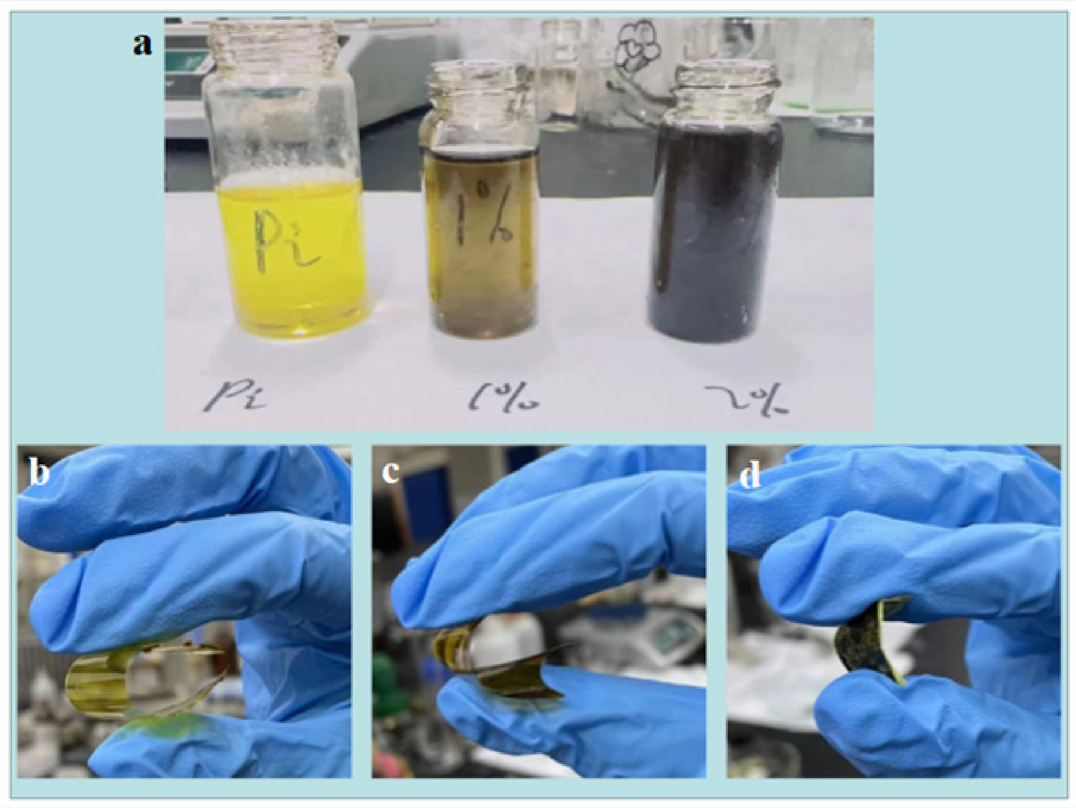

Figure 2: The pictures of PAA (a), PI/GO-1 % (b), PI/GO-2 % (c) and PI/3D graphene(d) composite films.

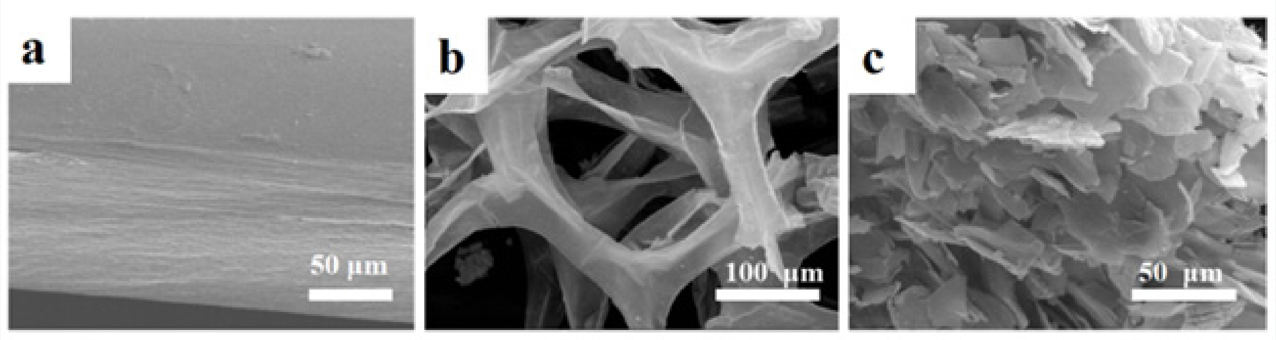

Figure 3: SEM images of PI (the surface and sides), 3D graphene and GO.

The TEM images of 3D graphene and GO are shown in figure 4. As shown in figure 4a, the basic outline of the graphene sheet can be observed. The detailed surface morphology of the GO can be observed, and the surface folds and undulations can be clearly seen, in figure 4b. The Raman spectra of 3D graphene and GO are shown in figure 5. As shown in figure 4, there are significant peaks D and G existed in 1360 cm^{-1} and 1610 cm^{-1}. Peak D in 1360 cm^{-1} corresponds to the internal defects of graphene, and peak G in 1610 cm^{-1} represents the structural integrity of graphene [13].

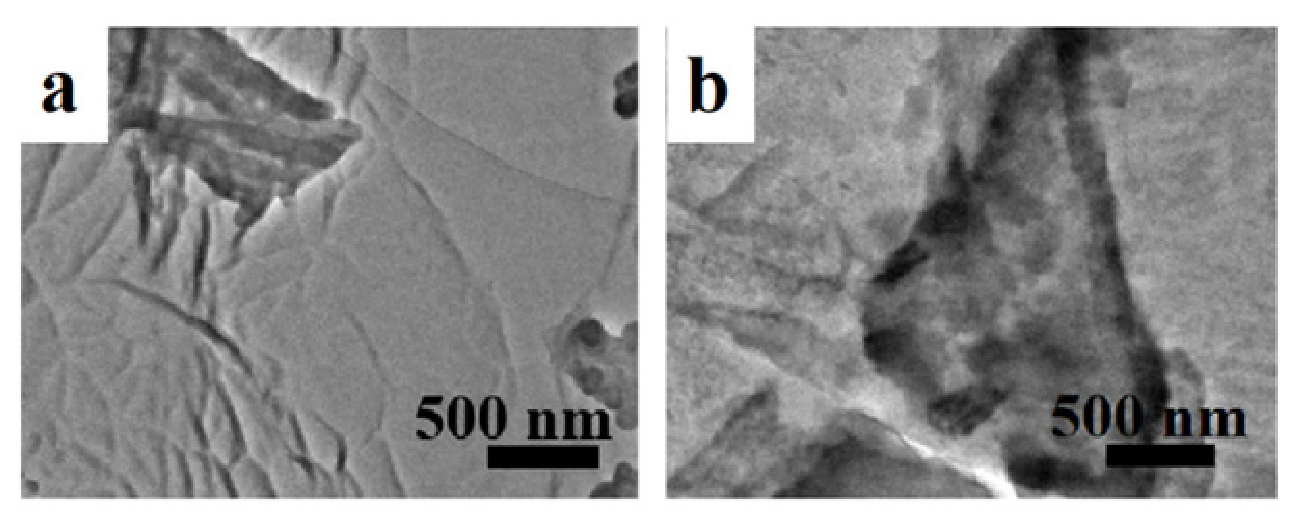

Figure 4: TEM images of 3D graphene and GO.

As shown in figure 6, there are Fourier transform infrared transform spectroscopy of PI/GO-2 % and PI/3D graphene composite films. Combining the spectra of two films, we can learn that the position of PI is in the C=O symmetrical stretching vibration absorption peak near 1734 cm^{-1}, the C=O asymmetric stretching vibration absorption peak near 1789 cm^{-1}, and the C-N axis near I369 cm^{-1}, the C=O bending vibration absorption peak near 726 cm^{-1} [14,15]. Infrared spectroscopy analysis results show that PAA/GO-2 % and PAA/3D graphene have been successfully imidized into PI/GO-2 % and PI/3D graphene film. Figure 7 shows the SEM image of cross-sections of PI/3D graphene and PI/GO-2 % thin film. As shown in figure 5a, there is a uniform distribution of three-dimensional graphene sheets, and no obvious phase separation phenomenon. Since the three-dimensional graphene can be closely connected with PI matrix to form many “Micro Capacitors” with Pl matrix, which is more beneficial for functioning the electrical properties of graphene to improve the dielectric properties of film. As shown in figure 7c, GO and PI matrix are combined to form a layered structure, which happens with significant layering phenomenon, and insufficient combination tightness, failure to play the electrical properties advantages of graphene sheets.

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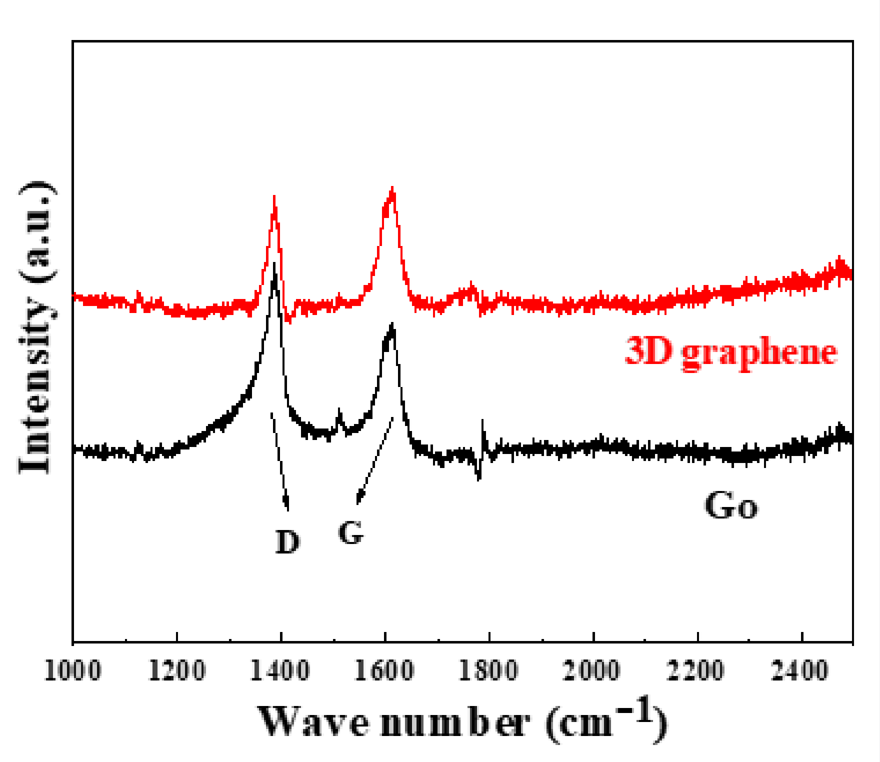

Figure 5: Raman scattering spectra of 3D graphene and GO.

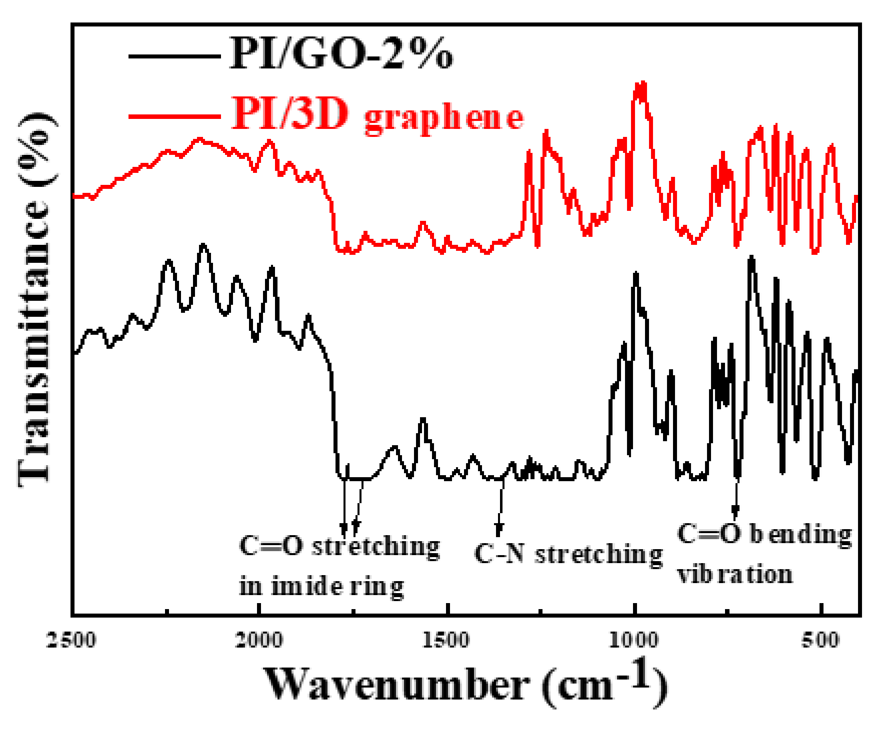

Figure 6: FT-IR spectra of PI/3D graphene and PI/GO-2 % composite films.

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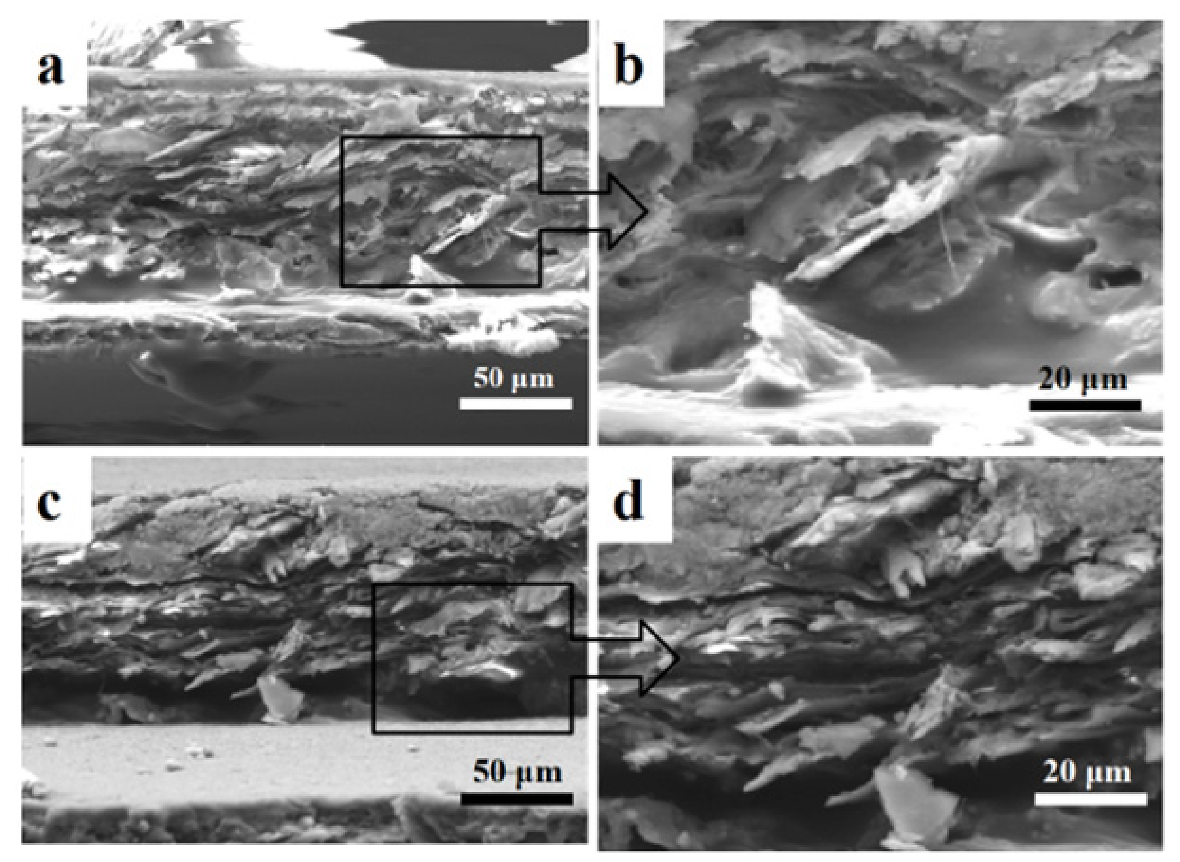

Figure 7: SEM images of cross-sections of PI/3D graphene and PI/GO-2 % composite film.

Figure 8 shows the dielectric constant and the dielectric loss of PI/Go composite films with changed frequency of applied electric field at room temperature, with the test frequency of 1-106 Hz. As shown in Figure 8a, the dielectric constant of the mass composite film of GO increases with the increase of GO content. When GO is increased to 1%, the dielectric constant of the composite film is 5.8 under the frequency of 1 Hz, which is 1.7 times higher than that of pure PI (3.36); when GO is further increased to 2 %, the dielectric constant of the composite film is 10.6 under the frequency of 1 Hz, which is 3.1 times higher than that of pure PI (3.36). As shown in figure 8a, the dielectric loss of composite film increases with the increased content of GO. The dielectric properties of PI/Go composite film can be interpreted by the conductor/polymer percolation threshold model. The percolation threshold theory holds that the electrical properties of polymer matrix materials dominate the electrical properties of composite materials when the content of conductive particles is small after adding the conductive particles to insulating materials; with the increased content of conductive particles, the filler gradually forms irregular clusters in the matrix. When the filler is increased to a certain concentration, there are more and more cluster particles, and the particles are connected with each other within a certain range, and the composite materials start to change from the insulator to the conductor. However, when the large-scale overlapping and joining system is going to be formed or has not been formed, the composite material happens a high dielectric transition, representing an increased dielectric constant, or even increased scope with several orders of magnitude. The characteristics of dielectric constant of the conductive/insulating system can be described by following power exponential equation:

$$\varepsilon = \frac{\varepsilon_0}{|(f_0 - f_{filler})/f_0|^{-q}}$$

Where, f_{filler} and f_0 are the volume fraction and percolation threshold concentration of filler in polymer matrix respectively, f_0 is closely connected with the microstructure of composite materials; ε_0 is the dielectric constant of polymer matrix; q is the scale constant, concerning on the material properties, microstructure, and phase to phase connectivity in composite system [16].

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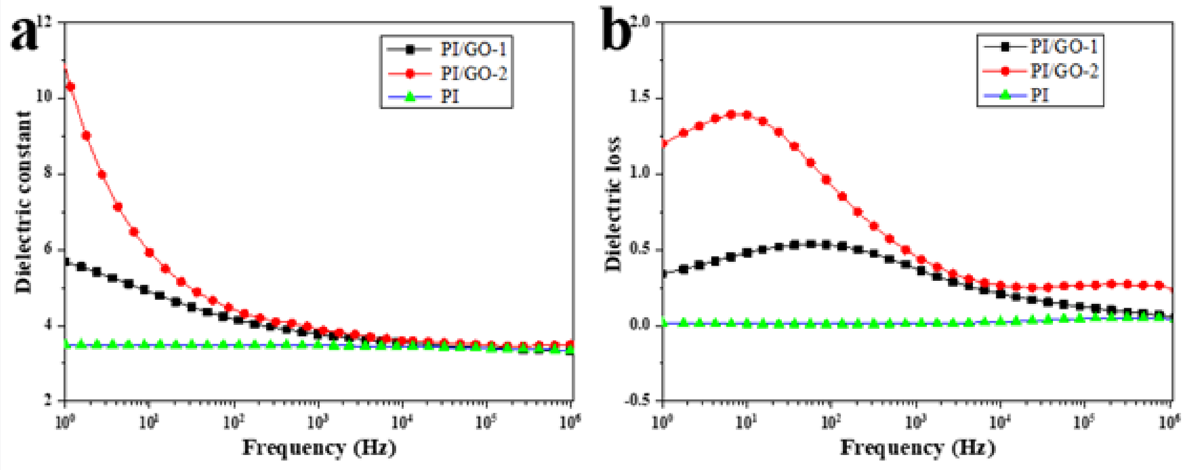

Figure 8: Dielectric constant and dielectric loss of PI/Go composite films.

The change of dielectric constant and dielectric loss of film is not significant when the content of GO is small (1%), where a small number of functional groups on GO surface and PI combine with a weak force to form a layered structure. However, influenced by a far distance between the layers, there fails to an effective capacitor network. Go has an insufficient influence on dielectric properties of matrix and keeps a basic stable status in the range of 100 ~ 106 Hz. With the further increased content of GO to 2 %, the dielectric constant and loss of thin film begin to increase at low frequency, which is because there are more and more PI/GO layered structures, the interface polarization increases, and the loss also increases. However, there fails to form a large-scale capacitor network, with insufficient influence on the dielectric constant.

Figure 9 shows the relationship between the dielectric constant and the dielectric loss of PI/3D graphene composite film with changed frequency of applied electric field at room temperature. As shown in Fig. 9, the ratio of dielectric constant of graphene to that of pure polyimide (3.36) is significantly increased since the formation of a conductive network between graphene sheets. Meanwhile, when the frequency of the applied electric field increases, the response of the capacitor network cannot keep up with the change of the electric field due to the limitation of the interface polarization time, resulting in the decrease of the dielectric constant and the dielectric loss with the increase of the frequency. Moreover, due to its three-dimensional graphene forming a relatively stable network structure in polymer matrix, the change of dielectric constant with frequency is smaller than that of PI/Go composite film, with a more stable structure.

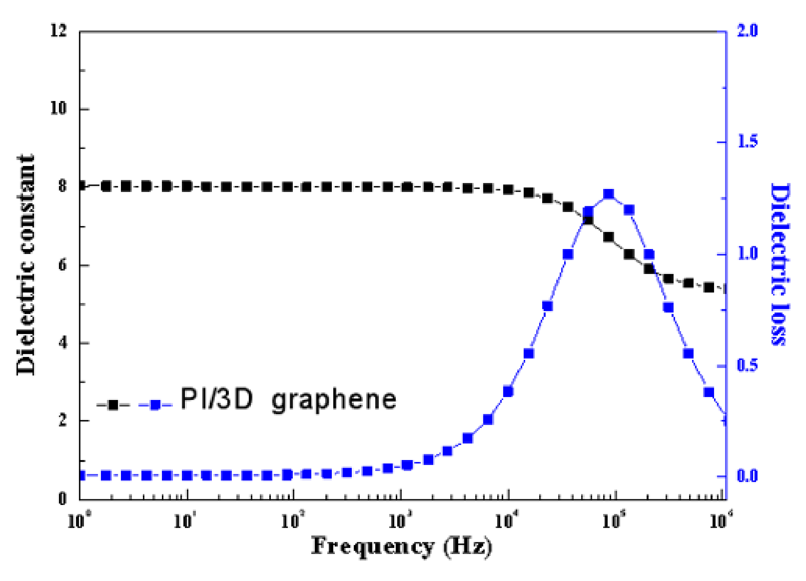

Figure 9: Dielectric constant and the dielectric loss of PI/3D graphene composite film.

Figure 10 lists the tensile strength of composite materials. As shown in figure 10, the tensile strength of all composite materials exceeds that of pure PI, and the adding of GO and three-dimensional graphene significantly improves the mechanical properties of composite materials. Meanwhile, with the increased GO addition, the strength and modulus of composite materials increased. However, PI/3D graphene composite film has a better mechanical property. When the content of GO is 1 %, the tensile strength of PI/GO-1 is 116.6 MPa, which is more than twice that of pure PI; and when the content of GO is 2 %, the tensile strength of PI/GO-2 is 100.3 MPa, which is slightly declined than that of PI/GO-1. This is because graphene has a monatomic layer honeycomb layer structure formed by carbon-carbon double bond connection, which makes graphene extremely hard. However, when the content of graphene increases, it is easy to form agglomeration in polymer matrix, causing the declined mechanical properties. Since its unique three-dimensional network structure, three-dimensional graphene in matrix polymer has a good dispersion in polymer matrix, which is an important factor in improving the mechanical properties of PI/3D graphene composite film.

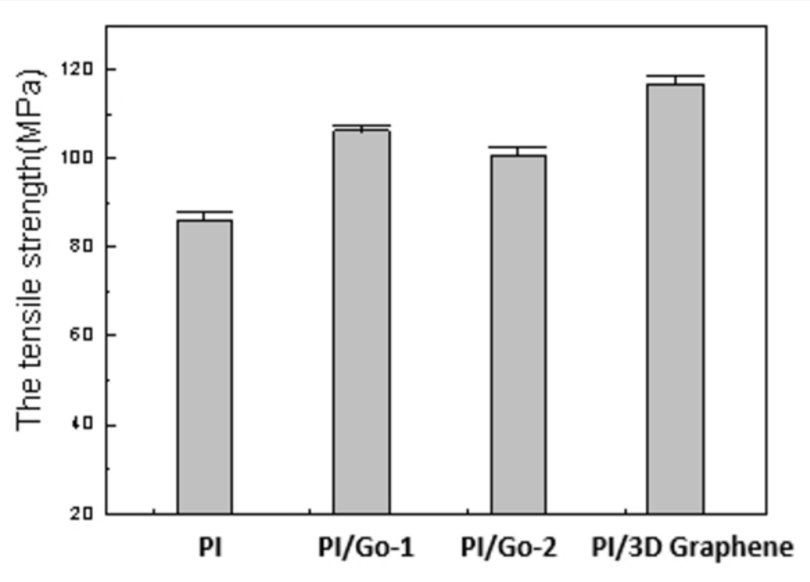

Figure 10: Mechanical property of composite films.

Conclusion

As a dopant, three-dimensional graphene can be dispersed in polymer matrix to prepare graphene/ polyimide composite materials with higher dielectric constant. Three-dimensional graphene can be closely connected with PI matrix, and units with PI matrix to form many “Micro Electric Containers”, which is more beneficial for functioning the electrical properties advantages of graphene and improving the dielectric properties of film. In the meanwhile, the uniform dispersion of the three-dimensional network structure in polymer matrix is of certain function in preventing graphene sheet stacking during the polymerization process. The doping of three-dimensional graphene not only increases the dielectric properties of polymer materials, but also improves the mechanical properties of composite materials. These composite films are flexible and meet the basic requirements of flexible materials.

Research Highlights

a) We report a simple strategy to prepare 3D graphene by chemical vapor deposition (CVD).

b) Polyimide (PI)/graphene oxide and PI/3D graphene composite films were produced by the in-situ polymerization.

c) PI/3D graphene exhibits significantly superior the dielectric and mechanical properties.

d) The doping of 3D graphene not only improves the dielectric and mechanical properties of composite materials.

Acknowledgement

The authors acknowledge financial support from Research Fund for the Doctoral Program of Higher Education of China (JMSUBZ 2020-02), Fundamental Research Funds for the Central Universities of Heilongjiang Province of China (2021-KYYWF-0554), Fundamental Research Funds for the national project cultivation project of Jiamusi University (JMSUGPZR2022-18)..

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