

Enhanced dielectric performances for graphene/polyimide composites by in situ controllable reduction of graphene oxide

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Abstract: Graphene/polyimide composites with excellent dielectric performances and mechanical properties were fabricated through in situ controllable reduction of graphene oxide (GO) during the composites processing, in which the reduction extents of GO were tailored by adjusting the proportion by weight of GO and the reducing reagent, 1,4-diiodobutane. The effects of the reduction degrees of GO on the dielectric and mechanical properties of graphene/polyimide composites were investigated via broadband dielectric spectroscopy and universal testing apparatus, respectively. The results showed that the dielectric constants of graphene/polyimide composites were significantly enhanced with the increasing of the reduction extents of GO. Moreover, the mechanical properties of the composites were also distinctly improved. Hence, the in situ controllable reduction of GO should be quite an ideal method for the fabrication of high dielectric constant composites.

1. Introduction

The graphene/polymer composites with high dielectric constants have drawn increasing interest in recent years for their applications in thin-film capacitors, super-large-scale integration and transistors due to their easy processing, mechanical flexibility and stable thermal properties.¹ However, homogeneous dispersion and interface interaction between graphene and polymer matrixes seem to be the key challenge on account of the pronounced tendency to agglomerate of graphene during the fabrication and processing of graphene/polymer composites.² Compared with graphene, graphene oxide (GO) bearing many oxygen-containing functional groups on the basal planes and edges, can be well dispersed in polymer matrix. However, in order to restore the electrical conductivity of graphene, the reduction process from GO to reduced graphene oxide (RGO) is necessary.³

In our previous work, we reported a new reducing agent, iodoalkane, which was applied to the fabrication of graphene/PI composites with high conductivity via in situ chemical reduction (ISCR) process.⁴ The reduction ability of iodoalkane is enough to recover the electrical conductivity of graphene. On this basis, we further research the impact of the reduction extent of GO on the dielectric properties of polyimide composites by adjusting the proportion by weight of GO and reducing agent, 1,4-diiodobutane.

2. Experimental

2.1 Preparation of RGO/PI composites.

From our previous work, the graphene nanosheets were easy to form conductive network by in situ reduction at 1.5 wt% loading in polyimide matrix, which was regarded as the percolation threshold.

Hence, we choose a relative low filler (1.0 wt% GO) content. All the composite films containing 1.0 wt% GO were prepared by in situ polymerization.⁴ RGO/PI composite films were prepared as follows:

The graphite oxide powder were dispersed in DMAc under ultrasonication for 12 h to obtain a 0.2 wt% GO dispersion. A three-necked flask equipped a nitrogen inlet was charged with a mixture of 4,4'-oxydianiline (2.428 g, 0.012 mol), GO dispersion (28.00 g) and *N,N*-dimethylacetamide (26.00 g). After stirring at 0 °C for 1 h, BPDA (3.572 g, 0.012 mol) was added and stirred at room temperature for 12 h, affording GO/polyimide acid (PAA) solution. To the GO/PAA solution, 1,4-diiodobutane (0.112 g) was added and stirred for 1 h. Free standing films were prepared by traditional solution casting method. The resulting mixture was casted on the glass substrate, followed by thermal imidization at 70°C for 5 h, and then at 100, 150, 200, 250 and 300 °C each for 1 h to obtain RGO-2/PI composite. In order to achieve the different reduction degrees from GO to RGO, the proportion by mass of GO and 1,4-diiodobutane was adjusted from 1 : 2 to 1 : 4, 1 : 6 and 1 : 8. The corresponding RGO/PI composites were denoted as RGO-2/PI, RGO-4/PI, RGO-6/PI, RGO-8/PI, respectively.

For comparison, the GO/PI composite films and pure PI films were also prepared by the above-mentioned experimental steps without the addition of reducing agent. The thicknesses of obtained composite films varied between 30 and 50 μm.

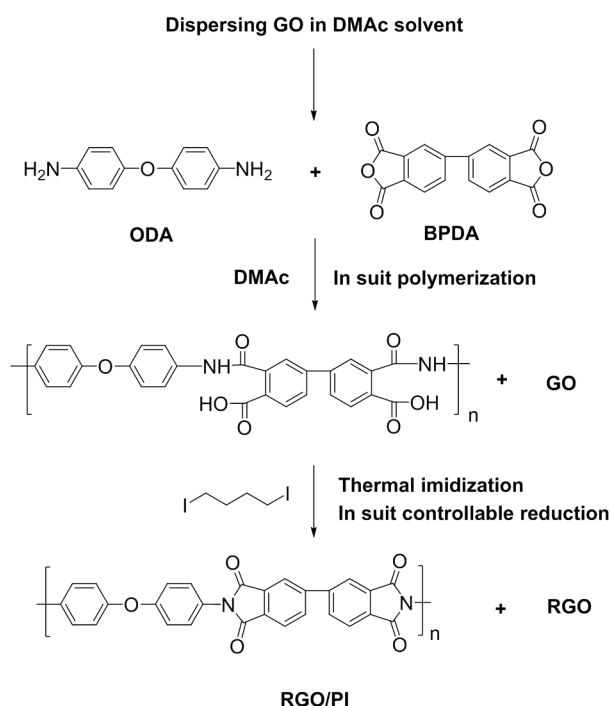


Fig. 1. The fabrication of RGO/PI composites via in situ controllable reduction.

3. Results and discussion

3.1 Dielectric properties of RGO/PI composites.

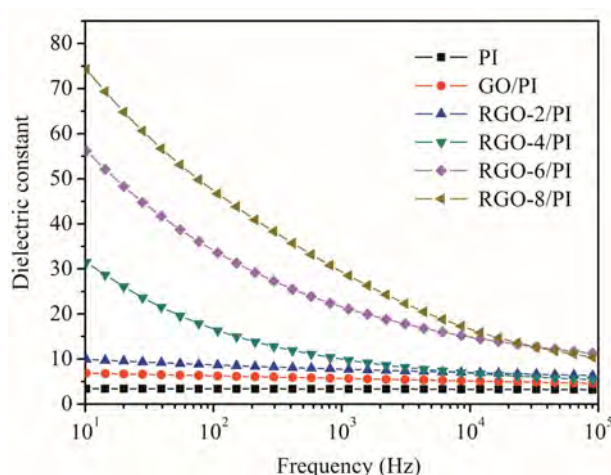


Fig. 2 Dependence of dielectric constants on the frequency for PI, GO/PI and RGO/PI composites.

Fig. 1 shows the dielectric constant of pure PI, GO/PI and RGO/PI composites with different frequency at room temperature. The dielectric constant of the GO/PI composite slightly increases as compared to pure PI. However, the dielectric constants of RGO/PI (RGO-2/PI, RGO-4/PI, RGO-6/PI, RGO-8/PI) appear significant increase with the mass ratio of GO/1,4-diodobutane increasing from 1 : 2 to 1 : 8. Especially, when the mass ratio of GO/reducing agent achieve 1 : 8, a high dielectric constant of 75 was obtained at the frequency of 10 Hz, which was almost 25 times than that of the pure PI films. The results should be attributed to the fact that the graphene structure has been partially restored by in situ reduction of GO within polyimide matrix. Meanwhile, by controlling the proportions of reducing agent, RGO/PI composites with various dielectric properties could be designed and prepared by virtue of the in suit controllable reduction of GO.

3.2 Mechanical properties of RGO/PI composites.

Table 1 Summary of mechanical properties of the pure PI, GO/PI and RGO/PI composite films.

	Tensile strength (MPa)	Tensile Modulus (GPa)	Elongation at break (%)
PI	106±3	2.0±0.4	23.0±7
GO/PI	152±6	2.4±0.2	18.4±5
RGO-2/PI	163±7	2.4±0.3	18.4±3
RGO-4/PI	150±4	2.6±0.4	12.6±2
RGO-6/PI	144±7	2.6±0.3	11.8±3
RGO-8/PI	137±5	2.3±0.3	10.4±3

Tensile testing was carried out to investigate the effects of the reduction extent of GO on the mechanical properties of RGO/PI composites. The tensile measurements summarized in Table 1 demonstrate that the GO/PI and RGO/PI films exhibit superior mechanical properties as compared to pure PI films. The tensile strength of the GO/PI films containing 1.0 wt% GO is increased up to 152 MPa from 106 MPa (about 41% higher than that of pure PI films). After the in situ reduction of GO by 1,4-diodobutane, the tensile strength of RGO/PI films still exceed the value of PI. Compared with PI, the tensile strength of RGO-2/PI films was increased by 54%. The further reduction of GO in

polyimide matrix resulted that the increased levels of the tensile strength of RGO/PI composites are gradually declined. However, even the tensile strength of RGO-8/PI film is higher than that of PI film. Moreover, the tensile modulus of RGO/PI films also showed a similar trend to the tensile strength with an increasing proportion of the reducing agent. All the results indicated that the incorporating GO into the polyimide matrix can observably improved the mechanical properties of the composites owing to the combing effect of the mechanical strength of GO and the interfacial interaction between GO and PI. When the reduction degrees of GO reached a critical extent, the decrease of the oxygen functional groups of RGO weakened the interfacial interactions between RGO nanosheets and PI chains.

3.3 Morphological of RGO/PI composites.

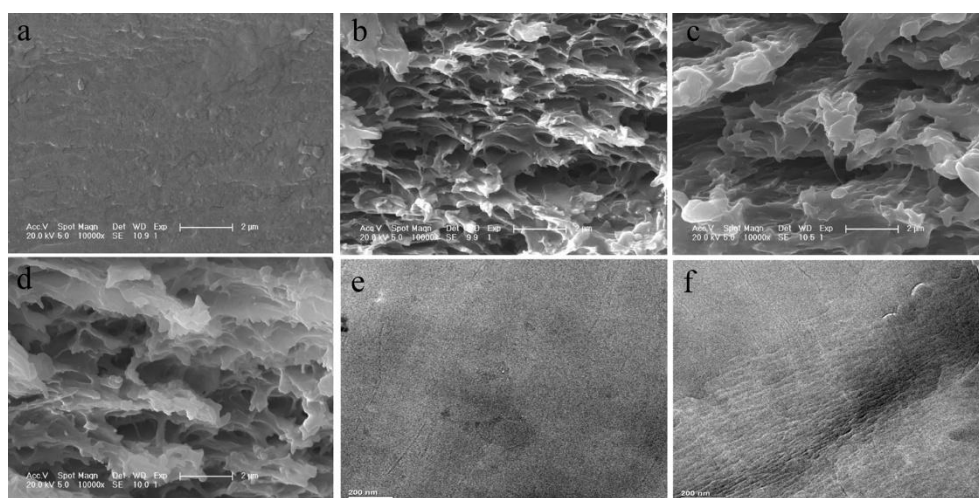


Fig. 3 SEM images of the fracture surfaces (a) pure PI, (b) GO/PI, (c) RGO-4/PI, (d) RGO-8/PI and TEM images of (e) GO/PI, (f) RGO-4/PI.

To further investigate the interfacial interaction between RGO and PI matrix and evaluate the dispersion and compatibility of RGO in polymer matrix, the fracture surfaces and the ultrathin sections of pure PI, GO/PI and RGO/PI films were observed by SEM and TEM, respectively. Fig. 5a show the SEM image of the neat PI fracture surface exhibits a smooth surface, indicating typical brittle fracture characteristics. However, the fracture surfaces of the GO/PI and RGO/PI composites all appear relatively rough as compared to pure PI films (Fig. 5b, 5c and 5d). The rough surface indicated the strong interfacial interaction between GO or RGO and PI, as well as fine dispersion of GO and RGO in PI matrix, which were favorable to the stress transfer from the polyimide matrix to the graphene nanosheets.

The TEM images of the GO/PI and RGO-6/PI composites show the uniform dispersion of GO and RGO in the PI matrix without large agglomerates formed. Especially, the fine dispersion of RGO indicated that the in situ reduction process had little impact on the dispersion of the GO sheets in the PI matrix. Such homogenous dispersion of RGO was beneficial to enhance the dielectric constant and the mechanical properties.

In summary, we have demonstrated that GO can be in situ reduced in polymer matrix and the reduction extents of GO are tailored by adjusting the proportion by weight of GO and reducing agent. With the reduction extent of GO increased, the dielectric constants of the composites were gradually enhanced. Hence, a series of RGO/PI composites with varied dielectric properties were prepared by

the controllable in situ reduction. Meanwhile, the mechanical properties of RGO/PI films were also improved as compared to PI.

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