



Dielectric properties of photocrosslinkable polyimide/functional graphene oxide composites



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ABSTRACT

Functional graphene oxide (FGO) with photosensitivity was incorporated into the photosensitive polyimide (PSPI) matrix via solution blending, to prepare the photocrosslinkable nano-composite films. The crosslinked composite films were obtained through UV irradiation. FGO was well dispersed in PSPI matrix and effectively covalently bonded to PSPI main chains through photo-chemical reaction. Due to the confine of electronic polarization caused by the crosslinked structure, the dielectric constant (k) and dielectric loss tangent ($\tan \delta$) of the crosslinked PSPI/FGO films decreased effectively, which could be tuned by varying both the UV irradiation time and FGO loading. Among all the composite films, the film with 0.5 wt% FGO content exposed under UV light for 900 s had the lowest k (2.58) and $\tan \delta$ (0.026) values at 10 MHz. These findings suggest that PSPI/FGO composite films are promising application in the field of photoresist with low dielectric constant.

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1. Introduction

Compared with the conventional polyimide, the photosensitive polyimide (PSPI) has some competitive advantages in application in the field of microelectronics. These advantages include simplifying the fabrication of the insulating interlayer and retaining the properties of the conventional polyimide [1]. Several kinds of PSPI based on α , β -unsaturated carbonyl, benzophenone, thioxanthone, and cinnamate have been prepared. Among them, the α , β -unsaturated carbonyl and its derivatives have well been studied for the synthesis of PSPI thanks to their high sensitivity to UV irradiation ($\lambda = 300\text{--}360$ nm) [2]. Although PSPIs may basically meet the demands of microelectronic industry, it is still attracted attention for developing new type advanced PSPIs with improving the mechanical properties and dimensional stability, as well as lowering dielectric constant and dielectric loss [3]. As one of the graphene-based materials, graphene oxide (GO) has the wide potential for functionalization, and its functional products are often served as reinforced nano-fillers used in polymer composites [4]. Besides, functional graphene oxide (FGO) endows polymer composites with some novel chemical and physical properties, for instance gas permeability, flame-retardance and optic-electronic properties [5]. To date, plenty of investigations about polyimide hybrids with GO or FGO have been reported, and the most of them

paid close attention to the non-photosensitive polyimide. And due to the low k value of GO paper (approximately 2.0 at 1 MHz) [6], some PI composites containing GO derivatives readily showed the low dielectric constant [7]. The photosensitive PSPI/FGO composites have rarely been reported. In this study, FGO was prepared by functionalizing GO with 1,5-bisaminophenyl-1,4-pentadien-3-one (BAPO) which supplies photosensitivity for GO, then FGO was dispersed in DMF solution of pre-synthesized PSPI containing BAPO units, to prepare photocrosslinkable composite films. The PSPI/FGO composite films with the tunable dielectric properties were obtained through UV irradiation.

2. Experimental

GO was prepared by using the improved Hummers' method [8]. 1,5-Bisaminophenyl-1,4-pentadien-3-one (BAPO) was prepared as described in the literature [9]. 4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA), N,N-dimethylformamide (DMF), pyridine and acetic anhydride were dried prior to use. FGO was firstly prepared through the amidation reaction between the carboxyl groups of GO and arylamine groups of BAPO. The precursor of PSPI was pre-synthesized through the polycondensation of BAPO and 6FDA at room temperature. Chemical imidization in the present of pyridine and acetic anhydride was conducted to obtain PSPI. PSPI/FGO composites, acquired in advance via solution co-blending, were poured onto a glass substrate and evaporated

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under vacuum for preparing PSPI/FGO composite films. Finally, the crosslinked PSPI/FGO (cPSPI/FGO) composite films were prepared by UV-curing. The cPSPI/FGO composite films with different FGO loadings (0.1, 0.2, 0.3, 0.5 and 1.0 wt%) were all prepared through the above processes. The detail information was given in [Supplementary information](#).

3. Results and discussion

The structure of FGO was characterized with multiple spectra ([Fig. 1](#)). As shown in [Fig. 1\(a\)](#), the shift of carbonyl band from 1734 cm^{-1} to 1640 cm^{-1} confirms the conversion of carboxyl in GO to amide group. Moreover, the stretching vibration of C=C from pentadienone unit in BAPO is signified by the absorption band around 1589 cm^{-1} . XPS analysis spectra of GO and FGO are shown in [Fig. 1\(c\)](#), where exists an observable increase in the N1s peak intensity (atomic fraction is 5.36%). Besides, an additional peak at 285.3 eV from C–N bond is presented in C1s spectra of FGO ([Fig. 1\(d\)](#)). Furthermore, the interlayer distance of FGO increases to 9.7 \AA compared with that of GO (8.5 \AA), according to the X-ray diffraction ([Fig. S1\(a\)](#)). All of the characteristic results mentioned above indicate that BAPO is successfully attached into the GO surface and the greater structural heterogeneity is consequently introduced in FGO sheets. The wafery, crumpled and transparent morphologies of FGO are observed in AFM ([Fig. 1\(b\)](#)) and TEM ([Fig. S1\(b\)](#)) images, respectively. The thickness of FGO shown in [Fig. 1\(b\)](#) is about 0.85 nm , indicating that exfoliation of FGO down to individual nanosheets is indeed achieved [10].

The UV–vis spectra of FGO, PSPI and PSPI/FGO films based on the different UV irradiation time are given in [Fig. 2](#). The maximum absorption peaks (λ_{max}) of FGO, PSPI and PSPI/FGO, corresponding

to 351, 330 and 338 nm respectively, are observed and all attributed to the $n-\pi^*$ transition from the pentadienone unit in BAPO. The strong blue shift at λ_{max} of PSPI and PSPI/FGO compared to that of FGO is explained by the reduction of auxochrome (NH_2) number in BAPO. In the UV–vis spectra of those three samples, a continuous intensity decaying of absorption peak at their λ_{max} is observed as prolonging the irradiation time, which suggests that the [2+2] cycloaddition reaction between BAPO units occurs under UV irradiation [9]. Since the extent of photocrosslinking is equal to the rate of change of absorbance at λ_{max} , the extent of photocrosslinking for PSPI and PSPI/FGO composites films can be calculated from the UV–vis spectra and adjusted by the UV irradiation time ([Fig. S2\(b\)](#)), and finally approaches a balance values ($\sim 82\%$) after UV irradiation for 900 s [2]. Because both of FGO and PSPI possess excellent photocrosslinking performance, the photocrosslinking reaction of PSPI/ FGO composite films occurs not only between the PSPI molecule chains, but also between the polymer chains and FGO ([Fig. S2\(a\)](#)), or between FGO nanosheets [11].

The morphologies of fractured surface of cPSPI composite films are shown in [Fig. 3](#). As shown in [Fig. 3\(a\)](#), the fracture surface of neat cPSPI is relatively flat in contrast to the rough fracture surface of cPSPI/0.1 wt% FGO shown in [Fig. 3\(b\)](#). When increasing the FGO content to 0.5 wt% (given in [Fig. 3\(c\)](#) and (e)), the FGO sheets are still embedded in the polymeric matrix, which indicates the good dispersion and strong interfacial interaction between FGO and cPSPI matrix. However, when FGO loading is up to 1.0 wt% (given in [Fig. 3\(d\)](#) and (f)), the FGO sheets are partially pulled out from the matrix, where several agglomerates are formed in the matrix. To further demonstrate the functions between FGO sheets and PSPI, the mechanical and thermal properties are studied ([Table S1](#)). Due to the crosslinking structure and interactions between FGO and PSPI, the tensile modulus (up to 4.24 GPa), glass-

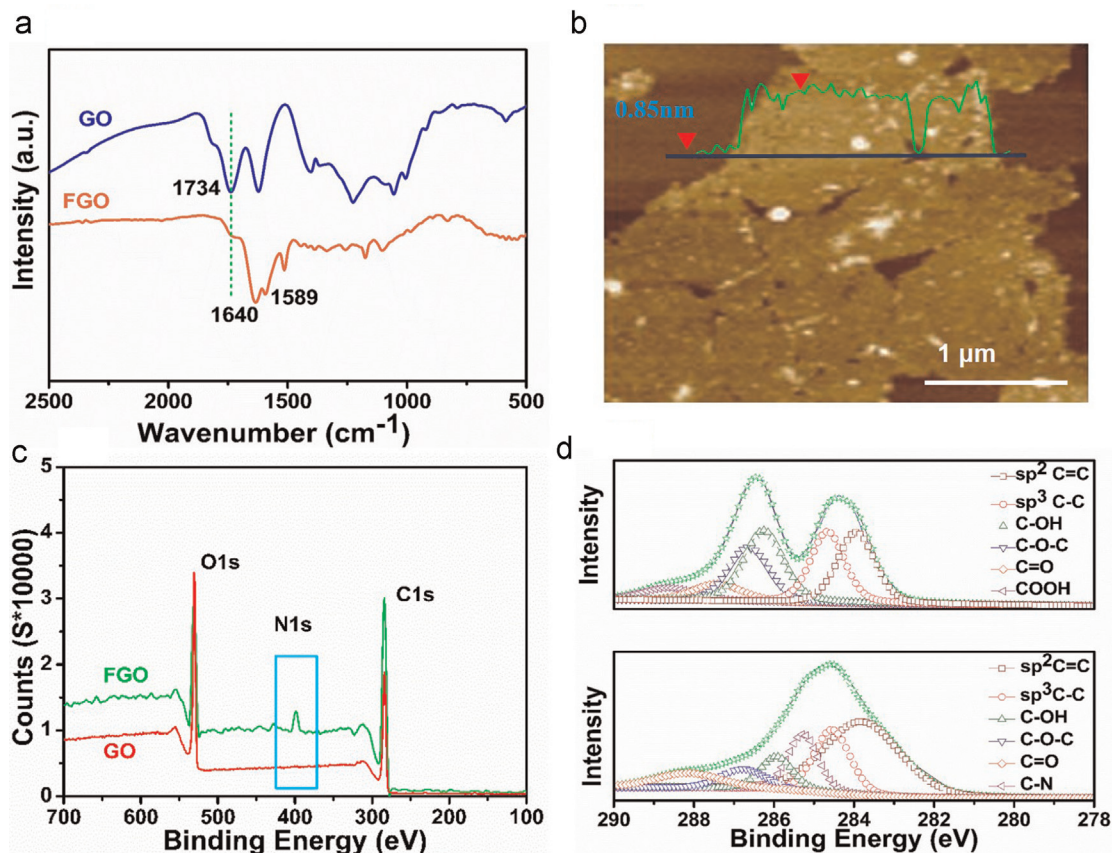


Fig. 1. (a) FT-IR spectra of GO and FGO, (b) tapping mode AFM image of FGO, (c) XPS survey scans of GO and FGO, and (d) high resolution C1s XPS spectra of GO and FGO.

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