

Transparent and Flexible Polyimide Composite Films with Improved Moisture Barrier Property by Graphene

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Introduction

Colorless polyimides (PIs) have been considered as potential substrates for flexible displays due to their excellent transparency, thermal stability, mechanical strength and flexibility. However, the high water/oxygen permeation of PI limits the performance or service life of those electronics using PI as substrates. In this study, we synthesize transparent and organo-soluble PI films from an alicyclic tetracarboxylic dianhydride BCDA and aromatic diamine 3,4'-ODA in the cosolvent of DMAc and GBL via one-pot process. In order to reduce the water-vapor-permeation-rate (WVTR), the high-aspect-ratio and thermally-reduced graphene oxide (RG) nanosheets were solution-blended with those PI in DMAc to fabricate the PI/RG composite films without the addition of coupling agent. For comparison, the as-synthesized graphene oxide (GO) nanosheets were also blended with the PI solution to prepare PI/GO composite films.

Results and Discussion

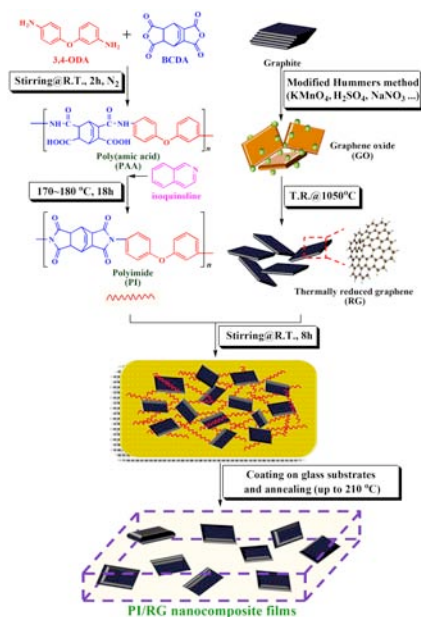
XPS (C1s) spectra of RG show the increased graphitic C=C components on RG [Figure 1a] indicating the successful thermal reduction of GO. In addition, the splitting of the C1s peak at higher binding energy suggests fewer oxidized carbon functional groups, C-OH or C-O-C, remained on RG after the thermal treatment on GO. The disappearance of the characteristic graphite peak at 26.4° in the XRD pattern of RG [Figure 1b] indicated the exfoliated feature of RG after the thermal reduction of GO. The ultra thin RG nanosheets with wrinkled, folded and silk-like morphology were observed together with the layered lattice structure of carbons in the edge or folding of RG. [Figure 1c]. The distribution of RG nanosheets with the features of high aspect ratio and high specific surface area in PI matrix [Figure 1d, 2] can effectively extend the path of the water vapor passing through the thin film and thus significantly improve water vapor barrier property. A dramatic decrease in WVTR by 93%, from 181 to 13 g/m²-day, was achieved upon the addition of only 0.1 wt% of RG in PI matrix [Figure 3]. A continuous decrease in WVTR with the increasing RG content was observed. The decrease in WVTR by GO was not as dramatic as RG because a more hydrophobic surface of PI/RG than that of PI/GO was observed at the same filler content. The contact angle of pure PI was 65° and increased with the presence of both GO and RG. Notably, the abundant functional groups on GO improved the dispersion in PI and affinity to PI matrix, the hydrophilic feature of GO led to less improvement in water barrier performance. Although the optical transparency of PI/RG decreased, the transmittance at 550 nm for PI film (thickness: 25 μm) containing 0.1 wt% of RG was still as high as 85 % [Figure 4]. An optimum combination of solvents DMAc and GBL in PI synthesis facilitates high optical transparency and strong mechanical strength simultaneously. The incorporation of tiny amount of RG reduced the coefficient of thermal expansion (CTE) to 48 ppm/°C for PI/RG-0.1 compared to 59 ppm/°C for pure PI. [Figure 5]. For pure PI, the modulus at initial 2% elongation was as high as 1 GPa and the elongation at break was more than 100% based on the tensile test results [Figure 6]. The PI films containing RG exhibited a similar modulus and a lower elongation while the RG content increased. The tensile strength of PI/RG was slightly higher than that of pure PI indicating the non-covalent interaction between PI and RG phases.

Conclusions

We have successfully prepared transparent PI films by using alicyclic tetracarboxylic dianhydride and asymmetric diamine monomers via one-step process. With the blending of small amount of ultra thin RG nanosheets in PI, the resultant PI/RG composites remain excellent optical transmittance and have enhanced mechanical strength and dimensional stability. Most importantly, RG forms excellent moisture barrier that the PI/RG nanocomposite is more hydrophobic and has improved resistance to water vapor compared to pure PI or PI/GO. With the addition of only 0.1 wt% of RG in PI, a dramatic reduction in the moisture permeability rate by 93% is achieved. The results suggested the synthesized flexible PI/RG composite films by a facile process are potential substrate materials for the applications in advanced touch panel or flexible display, where high optical transparency, sufficient water resistance and good thermal stability were essentially required.

Reference

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Scheme 1. Synthesis of PI/RG composite films

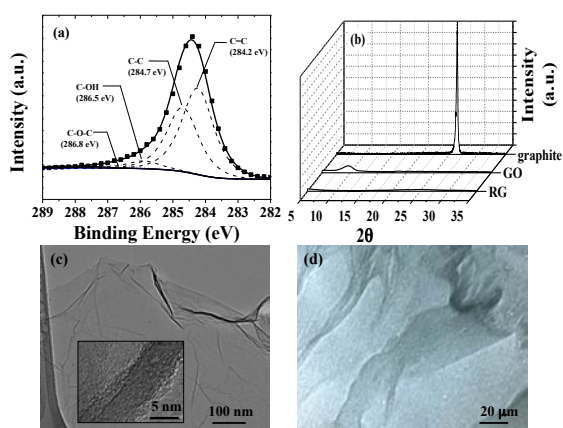


Figure 1. (a) XPS spectra of RG. (b) XRD patterns of graphite, GO and RG. (c) TEM image of RG. Inset: High-magnified TEM image of RG edges. (d) TEM image of PI/RG composite film.

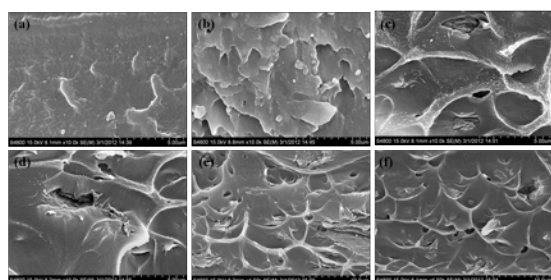


Figure 2. SEM images of the fracture surface of (a) pure PI, (b) PI/RG-0.1, (c) PI/RG-0.3, (d) PI/RG-0.5, (e) PI/RG-0.8, and (f) PI/RG-1.0. The scale bars in images (a-d) and (e, f) are 5 and 10 μm, respectively.

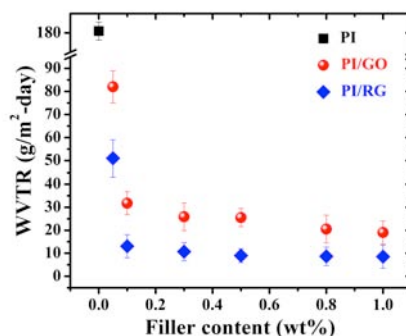


Figure 3. Effects of GO and RG contents on the water vapor transmission rate (WVTR) of PI/RG and PI/GO nanocomposite films. Note: The values were measured at 40 °C and 100% RH.

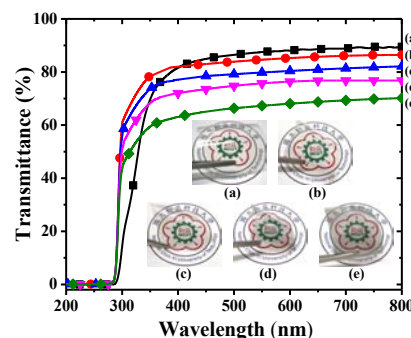


Figure 4. UV-vis spectra of (a) pure PI and (b) PI/RG-0.1, (c) PI/RG-0.3, (d) PI/RG-0.5, and (e) PI/RG-0.8 composite films. Inset: The digital photographs of PI films with the thickness of 25 μm.

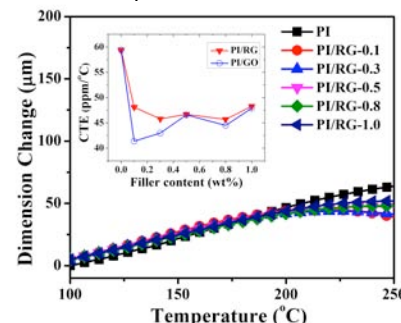


Figure 5. TMA curves of pure PI and PI/RG composite films. Inset: Effect of filler (RG or GO) content on the coefficient of thermal expansion (CTE) in the temperature range of 100 to 200 °C.

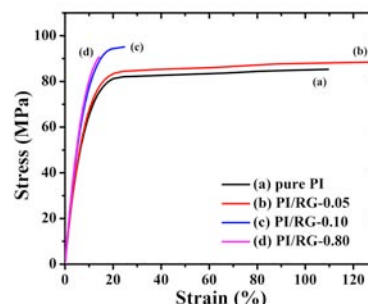


Figure 6. The tensile test results of pure PI and PI/RG composite films.