



# Effect of defect-healing in graphene nanosheets on the mechanical properties of polyimide nanocomposites

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## ABSTRACT

We report an effective method for fabricating graphene-based multifunctional polyimide (PI) nanocomposites via *in situ* polymerization, by the chemical defect-healing of pyridine functionalized reduced graphene oxide (H-Py-RGO). H-Py-RGO was successfully obtained through intramolecular cross-dehydrogenative coupling (ICDC). The mechanical properties, and thermal stability of the PI/H-Py-RGO nanocomposites were significantly improved compared with those of pristine PI film due to the restoration of the defect sites on the graphene surface, and the resulting high compatibility between the H-Py-RGO and the PI matrix. The tensile strength and modulus of the PI/H-Py-RGO nanocomposites with 1 wt% of added H-Py-RGO were increased by about 598% (883.5 MPa) and 535% (39.4 GPa) compared to those of pristine PI, respectively. Furthermore, 5 wt% H-Py-RGO loading resulted in a 91% reduction in the coefficient of thermal expansion (CTE) of the PI/H-Py-RGO nanocomposite.

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## 1. Introduction

Aromatic polyimide (PI) is a type of engineering plastic resin with a wide range of applications in automobiles, aerospace, optoelectronics, microelectronics, adhesives, and coatings, thanks to its excellent heat and chemical resistance, dimensional stability, and mechanical properties [1–5]. Despite numerous advantages, PI also has some limitations. Because of defects in its insulating nature, polyimide accumulates electrostatic charge, and degrades prematurely [6–9]. With the rapid development of advanced aerospace systems, PI resins with superior properties are now needed to meet complex material requirements. As an effective approach to overcome the inherent shortcomings of the polymers, in recent years, PI has been combined with carbon nanomaterials such as carbon nanotubes (CNTs) and graphene [10–15].

Graphene is a layered 2-dimensional (2D) nano-carbon allotrope, and as a filler material has been used to successfully improve the thermal, electrical, mechanical, and chemical properties of

polymers [16–18]. However, graphene-based polymer composites usually fail to achieve the expected level of mechanical reinforcement. The reinforcing efficiency of graphene depends greatly on the dispersion and distribution of the graphene sheets in the polymer matrix [19–21]. Unfortunately, pristine graphene tends to agglomerate within the matrix because of its low compatibility with organic polymers. In order to overcome this problem, many studies have investigated methods to functionalize the graphene surface, to improve the interfacial interactions between the graphene and PI matrix, thus enhancing the physical properties of the composites via *in situ* polymerization [22–26].

Recently, we developed PI nanocomposites using pyridine-functionalized reduced graphene oxide (Py-RGO) [27]. The pyridine groups on the RGO surface acted as a catalyst to enhance the mechanical and oxygen gas barrier properties of the PI nanocomposites. The positive effects can be attributed to the efficient dispersion and distribution of the graphene sheets due to hydrogen bonding with the PI matrix. In addition, by acting as a hydrogenation catalyst, the pyridine groups promoted imidization reactions in the PI nanocomposites.

Despite these advantages, disorder and defect sites can occur in the Py-RGO as a result of the synthesis process or corrosive chemical oxidation, and can strongly affect the physicochemical

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and mechanical properties of the Py-RGO after reduction. In particular, the intrinsic electrical conductivity of graphene highly depends on the quantity of defect sites present on its surface [28–30]. Disorder and defects in the RGO in polymeric matrices greatly limit the composites' practical application. For this reason, controlling defect sites is considered to be critical to tailoring the intrinsic properties of graphene. If the graphene lattice disorder and defects can be repaired and before being incorporated into the polymeric matrices, the resulting RGO composites could exhibit better mechanical reinforcement and improved electrical conductivity [31–34].

Herein, we propose an effective method of fabricating defect-healed graphene-based PI nanocomposites via *in situ* polymerization for high performance materials. The healing of chemical defects in the Py-RGO was carried out via intermolecular cross-dehydrogenative coupling (ICDC) with  $\text{FeCl}_3$ . This healing method can effectively promote the restoration of the  $\text{sp}^2$ -hybridized carbon network in Py-RGO, which reduces the number of defect sites in the Py-RGO, but also shows high dispersibility due to surface pyridine derivatives. A polymer nanocomposite filled with the defect-healed Py-RGO (H-Py-RGO) exhibited significantly enhanced mechanical properties as well as substantial reduction in the coefficient of thermal expansion. We have found that defects present in the basal plane of graphene are important factor affecting the strength of the composite materials and demonstrated that defect-healing is very helpful for improving the physical properties of polymer nanocomposites.

## 2. Experimental

### 2.1. Materials

Natural graphite (natural microcrystal grade, 99.9995%) was purchased from Alfar -Aesar (USA). The 4-Chloropyridine was purchased from TCI (Japan). Purified 3,3'-dihydroxybenzidine (DHB) and pyromellitic dianhydride (PMDA) were acquired from Wakayama Seika Kogyo (Japan) and TCI (Japan), respectively. Purified *N*-methyl-2-pyrrolidinone (NMP) was purchased from Sigma Aldrich (USA). Common organic solvents were purchased from Daejung (Korea). All of the chemicals were used without further purification.

### 2.2. Chemical defect-healing of pyridine functionalized reduced graphene oxide (H-Py-RGO)

H-Py-RGO was synthesized from Py-RGO, as reported in our previous study [27]. The detailed experimental procedures for synthesizing Py-RGO are described in the supplementary information section. H-Py-RGO was prepared from the Py-RGO as follows. 0.2 g of Py-RGO powder were dispersed in a 100 mL of dichloromethane. The mixture was then purged with nitrogen gas for 30 min. Then, a solution of 5 eq.  $\text{FeCl}_3$  in nitromethane was added dropwise to the reaction mixture in a nitrogen atmosphere over 2 h. The flask was sealed and the reaction was stirred at room temperature for 24 h before being stopped by the addition of 100 mL of methanol. The product was isolated by filtration, washed with methanol, and dried in a vacuum oven.

### 2.3. Preparation of PI/H-Py-RGO nanocomposites films

Pristine PI and PI/H-Py-RGO nanocomposites were prepared by the classical two step method. First, H-Py-RGO was dispersed into NMP in an ultrasonic bath for 1 h at 0 °C. Then, DHB was poured into the mixture and stirred for 30 min. After the ODA had completely dissolved, PMDA was added into the mixture. The mixture was polymerized after stirring overnight at room temperature. After

that, it was placed *in vacuo* for 1 h to remove air bubbles. The prepared H-Py-RGO incorporated poly(amic acid) (PAA) was cast onto a slide glass using a spin coater. The cast films were dried at 90 °C and 150 °C for 1 h *in vacuo*. The PAA nanocomposite film was thermally treated by gradually increasing the temperature up to 200 °C for 1 h, 250 °C and 300 °C for 30 min in a furnace, under a nitrogen atmosphere.

## 2.4. Characterization

The surface modification of H-Py-RGO was determined by X-ray photoelectron spectroscopy (XPS; K-alpha, Thermo SCIENTIFIC, USA) and Raman spectroscopy (LabRAM HR, Horiba, Japan). The thickness and lateral size of the H-Py-RGO sheets was characterized by atomic force microscopy (AFM; Park NX-10, Park systems, Korea). To observe the microstructures of the H-Py-RGO, transmission electron microscope (TEM; Tecnai, FEI, USA) was used at 200 kV. For the TEM sample preparation, H-Py-RGO powder was dispersed in deionized water, and subsequently the dispersion was dropped on a copper grid and air-dried. The electrical conductivity of each powder were measured using a powder resistivity measurement system (HPRM-A2, Hantech, Korea) at 2000 kg load. Fourier transform-infrared (FT-IR; Nicolet IS10, Thermo, USA) spectra of the samples were analyzed in the attenuated total reflection (ATR) mode. The fractured surface morphologies of the PI nanocomposite films were characterized by scanning electron microscopy (SEM; Nova Nano SEM, FEI, USA). The mechanical properties of the PI nanocomposite films were measured by a universal testing machine (UTM; Instron, USA). The mechanical properties of the samples, which were prepared at 0.5 cm in width and 2.5 cm in length, were measured at a testing speed of 5 mm/min. The coefficient of thermal expansion (CTE) was measured according to the ASTM E831 standard using a thermomechanical analyzer (TMA 402 F3, Netzsch, USA), and measurements were conducted under a tension mode (tension force 0.05 N), a heating rate of 10 °C/min, and a temperature range of 25–300 °C under a nitrogen atmosphere.

## 3. Results and discussion

### 3.1. Characterization of H-Py-RGO

The chemical defect-healing of Py-RGO was carried out through an ICDC reaction with the catalyst  $\text{FeCl}_3$  (Scheme 1). The H-Py-RGO was then investigated by XPS and Raman spectroscopy, AFM, and TGA analysis.

Fig. 1(a)–(b) shows the deconvoluted XPS C1s and N1s spectra of the H-Py-RGO. The H-Py-RGO showed several peaks at 284.8, 285.6, 286.1, 286.6, 287.1 and 287.6 eV, corresponding to  $\text{sp}^2$ ,  $\text{sp}^3$ , C–N, C–O, C=O, and O–C=O groups, respectively. The C–N binding peak confirms the presence of covalent bonds with a nitrogen atom on the surface of the H-Py-RGO. The deconvoluted N1s spectra also showed two peaks at 399.2 and 400.5 eV, corresponding to –N = and –NH– groups, respectively. The presence of the –N = bonds strongly indicates that pyridine functional groups were connected to the surface of graphene. The calculated surface elemental compositions of pristine GO, Py-RGO, and H-Py-RGO based on XPS results are listed in Table 1. The C/O ratio shows a very high content of oxygen species in the pristine GO (2.9%). In the RGO, the ratio was found to be (11.1–15.6%), confirming the successful reduction of GO. The calculated atomic percentage of the constituent elements shows that there were at least 3 times more nitrogen atoms in the Py-RGO and H-Py-RGO than in pristine GO, and these results imply the successful introduction of pyridine derivatives. Furthermore, the calculated peak percent area of the  $\text{sp}^3$ -hybridized carbon peak of H-Py-RGO decreased, and the amount of the

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