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Full Length Article

Methylpiperidine-functionalized graphene oxide for efficient curing acceleration and gas barrier of polymer nanocomposites

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ABSTRACT

We synthesized methylpiperidine-functionalized graphene oxide (MP-GO) by introducing 4-amino-1-methylpiperidine into reactive epoxy and/or carboxylic acid groups on pristine GO. Then, we applied the MP-GO as a curing catalyst for polyimide (PI) nanocomposites. The MP-GO was found to be an effective base-catalysts for the thermal conversion of polyamic acid (PAA) precursor to PI. Interestingly, when 3 wt% of MP-GO was added to the PI matrix, the complete imidization of nanocomposites was achieved at a temperature lower than 200 °C. In addition, the PI/MP-GO nanocomposite films exhibited reinforcement of the oxygen barrier properties which were even better than those of pristine PI, due to the excellent dispersion state of MP-GO and the favorable non-covalent interaction between MP-GO and the PI matrix. Comparison to pristine PI, the oxygen permeability of nanocomposite films that contained only 1 wt% of MP-GO loading was significantly decreased, by about 80%. Furthermore, all the PI/MP-GO nanocomposites exhibited high thermal stability.

1. Introduction

Polymer nanocomposites with well-defined architectures are attracting much attention because they have synergistic properties as well as tailored to specific industrial applications such as microelectronics, the aerospace industry, and optoelectronics [1–6]. Particularly in the area of nanocomposite reinforcements, polyimide (PI) nanocomposites made with carbon nanomaterials such as carbon black [7], carbon nanotubes [8,9], graphene [10–13], and carbon nanofibers [14,15] have recently drawn considerable interest owing to their exceptional mechanical strength, electrical conductivity, thermal stability, and gas barrier properties.

Among these carbon families, graphene oxide (GO), an oxidized version of graphene presenting epoxides, hydroxyls, ketones, and carbonyl on its edges and surface, has been employed in biosensors, catalysts, composites, membrane, and coatings due to its unique and physicochemical properties [16–19]. Although GO sheets have high solubility in water and polar organic solvents owing to their hydrophilic nature, they have some limitations such as low compatibility with most organic polymers, which can reduce the reinforcing effects in the polymer matrix [20–23]. Given the above issues, to produce high quality graphene polymer composites (GPCs), it is important to design and synthesize customized GO-derived materials in ways that the interface between the GO and polymer matrix can be modulated using various approaches.

Recently, we reported graphene-derived PI nanocomposites which incorporated chemically functionalized graphene (CFG), and had a variety of organic functional derivatives on the surface of the graphene, to improve the dispersibility of a graphene in polymeric matrix [24]. The PI nanocomposite filled with CFG exhibited a considerably reinforced mechanical strength and gas barrier ability compared to pristine PI. However, it was necessary to treat it at a temperature of over 300 °C for full imidization of the PAA [25,26]. This high curing temperature may lead to several defects, which are produced by the partial destruction of the polymer and/or thermal elimination of organic functional groups on the filler surface during the transformation of the PAA precursor to the final PI product. Most importantly, not only might the physical properties of the PI nanocomposites deteriorate, but the components may also deteriorate when the PIs are used in industrial applications [27,28]. Therefore, lowering the curing temperature in the

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manufacturing process of the high-performance PI nanocomposites is highly desirable.

This study highlights an effective way to develop low temperature curable PI barrier nanocomposite films with high thermal resistance using methylpiperidine-functionalized graphene oxide (MP-GO). The MP-GO was prepared by a facile single step functionalization by the reaction of 4-amino-1-methylpiperidine with pristine GO. Afterwards, PI nanocomposites with different MP-GO loading were produced by *in-situ* polymerization, followed by thermal curing of the polyamic acid (PAA) precursor. The MP-GO could be well dispersed in well-known organic solvents such as *N,N*-Dimethylacetamide (DMAc) and homogeneously dispersed within a polymer matrix, because of the presence of methylpiperidine functional groups on the surface of the GO. In particular, the methylpiperidine groups, one of the effective base-catalysts, not only acted as a dehydrogenation catalyst for PI but could also effectively enhance the degree of imidization. Moreover, the homogeneous dispersion of MP-GO which can block the pathway of oxygen molecules within the PI matrix, can effectively improve the gas barrier property. All the PI/MP-GO nanocomposite films were found to exhibit high storage modulus and thermostability, which are of paramount importance in the field of GPCs.

2. Experimental

2.1. Materials

Natural graphite flakes (natural microcrystal grade, 99.9995%) were purchased from Alfar-Aesar (USA). The 4-amino-1-methylpiperidine, pyromellitic dianhydride (PMDA, > 99%), and 4,4′-oxydianiline (ODA, > 98%) were purchased from Tokyo Chemical Industry (Tokyo, Japan). *N,N*-Dimethylacetamide (DMAc) was obtained from Sigma-Aldrich (St Louis, MO, USA). Common organic solvents were purchased from Dae-Jung Chemicals (Siheung, Korea).

2.2. Synthesis of methylpiperidine-functionalized graphene oxide (MP-GO)

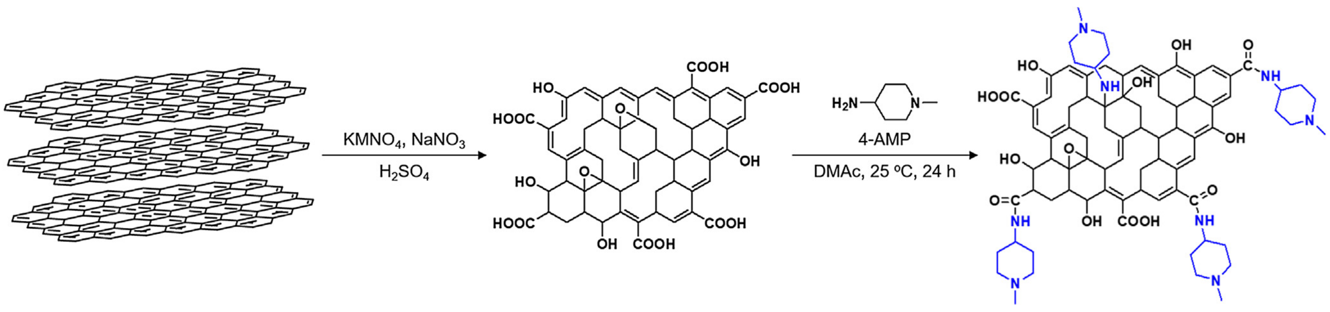
Scheme 1 depicts the preparation procedure for MP-GO. First, the pristine graphene oxide (GO) was prepared by oxidizing natural graphite flakes via modified Hummer′s method. The 2 g GO was immersed in a 100 mL of DMAc placed in a 250 mL four-neck flask and mechanically stirred and ultra-sonicated for 1 h. Then, 1 g of 4-amino-1-methylpiperidine was slowly added dropwise to the mixture and stirred at room temperature for 24 h. The unreacted 4-amino-1-methylpiperidine and impurities were filtered and washed with DMAc and ethanol. The resulting solid was re-dispersed in 200 mL of di-ionized water and freeze dried for 48 h. Finally, 2 g of MP-GO was successfully collected.

2.3. Preparation of PI/MP-GO nanocomposites

The precursor of PI, poly(amic acid) (PAA) was synthesized by solution polycondensation of ODA with PMDA at an equivalent molar ratio. The poly-condensation step was performed in DMAc under magnetic stirring for 24 h. The PI/MP-GO nanocomposite was fabricated via an *in-situ* polymerization and thermal curing process (Scheme S1). MP-GO was dissolved in DMAc using homogenizer at 1200 rpm for 30 min and further ultra-sonicated at 0 °C for 1 h. ODA was added in the suspension, followed by the gradual addition of PMDA. The resulting mixture was stirred for a prolonged period of 24 h in an inert atmosphere. The poly-condensation process was identical to that of the viscous PAA/MP-GO solution. After degassing with a vacuum pump, the resulting dark mixture was spin-casted at 500 rpm on clean glass substrates and then heated at 40, 80, 130, 160, 200, 250, and 350 °C for 1 h *in vacuo*.

2.4. Characterization

Fourier transform-infrared (FT-IR; Nicolet IS10, Thermo Fisher Scientific, USA) spectra were recorded with a scan range of 400–4000 cm^{-1}. X-ray diffraction (XRD) measurements were performed using a conventional X-ray diffractometer (Rigaku Miniflex, CuKα (λ = 1.5418 Å). Raman spectra were recorded from 1000 to 2000 cm^{-1} using a high resolution Raman spectrometer (LabRAM HR, Horiba Scientific, Japan). The X-ray photoelectron spectroscopy (XPS) spectra were recorded using a spectrophotometer (K-Alpha, Thermo Fisher Scientific, USA). The excitation source used for the survey spectra was standard Al Kα (1486.6 eV) at 14.9 keV anode voltage. 4.6 A and 20 mA were applied as the filament current and mission current, respectively. Transmission electron microscope (TEM; Tecnai, FEI, Japan) was operated at 2000 kV. The elemental mapping images of samples were scanned using energy filtered TEM. The samples were prepared for TEM analysis by drop casting graphene powder dispersed in di-ionized water on a carbon coated 150 mesh copper grid and air-dried. Scanning electron microscopy (SEM; Nova Nano SEM, FEI, USA) was performed at an acceleration voltage of 10.0 kV. The non-destructive technique, 3D X-ray computed tomography was performed using a Zeiss Xradia 510 Ultra/Versa hybrid system to visualize the internal features of the film. X-rays penetrate through the film, which was rotated up to 360° with at increments of 0.2° exposed for 4 s in a single projection beam. The power of X-ray microscopy (XRM) was 10 W with 60 kV. The resulting images were reconstructed by Carl Zeiss′s Object Research Systems (ORS) image analysis program. Thermogravimetric analysis (TGA) was performed under a nitrogen gas flow using a Q50 TA Instruments at a heating rate of 10 °C/min from 40 to 800 °C. Dynamic mechanical analysis (DMA) was conducted using a Q800 TA Instruments at a scanning rate of 3 °C/min with a load frequency of 1 Hz in air. The specimens were prepared in film form (30 mm length, 10 mm wide, and *ca.* 30 µm thickness). The oxygen transmission rate (OTR) of films was investigated at 0 RH% and 23 °C in accordance with the procedure described in ASTM International procedure D3985 using a commercial MOCON′s proprietary instrument (Ox-Tran system).



Scheme 1. Synthesis scheme of MP-GO.