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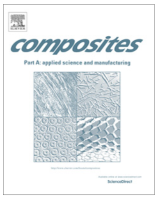

Click coupled stitched graphene sheets and their polymer nanocomposites with enhanced photothermal and mechanical properties

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ABSTRACT

The chemically stitched graphene oxide (GO) sheets were obtained using a click chemistry reaction between azide-functionalized GO and alkyne-functionalized GO. The click coupled GO (GO-click-GO) sheets showed the largely increased electrical conductivity and near infrared laser-induced photothermal properties compared to the GO sheets, which result from formation of triazole ring as a bridging linker between the GO sheets. The polyurethane (PU) nanocomposites incorporating the GO-click-GO sheets exhibited enhanced mechanical properties of breaking stress and modulus than the GO/PU nanocomposites. The modulus of GO-click-GO/PU nanocomposites was higher than that of the GO/PU nanocomposites at the same filler loading of 0.1 and 0.5 wt%. The GO-click-GO/PU nanocomposites also showed a significantly improved photothermal properties compared to the GO/PU nanocomposites at the same filler loading. The click coupled stitched GO sheets in this study can be used as the superior reinforcing fillers for mechanically and photothermally high performance polymer nanocomposites.

1. Introduction

Graphene has the superior mechanical, thermal, and electronic transport properties, and the defect-free graphene especially possesses a Young's modulus as high as about 1 TPa, breaking stress of over 100 GPa [1–3], thermal conductivity of about 5000 W/mK [4,5], and electrical conductivity of about 7000 S/cm [6,7]. Because of these extraordinary properties, the graphene has been considered to be the ideal reinforcing filler in polymer nanocomposites. However aggregation between the graphene sheets and insufficient exfoliation of layered graphenes have limited to manifest the superior properties of the graphene sheets in the polymer nanocomposites. Therefore the functionalized graphene with some organic groups or polymers and graphene oxide (GO) sheets have been more used to fabricate the well dispersed graphene/polymer nanocomposites [8–11]. However they have the inferior conductive networks between graphene sheets in the polymer nanocomposites because of presence of the non-conductively functionalized groups around the graphene sheets. Therefore the graphene functionalization with good electron transferring links may be desirable to improve the electrical and mechanical properties of the polymer nanocomposites.

Since the first introduction by Sharpless and coworkers [12], click chemistry has received much attention in the field of organic synthesis, chemical biology, and materials chemistry [13,14]. The click chemistry reaction between azide and alkyne moieties, also called as Cu-catalyzed Huisgen 1,3-dipolar cycloaddition has many advantages such as tolerance of water, high selectivity, simple reaction condition, and excellent yield. Recently the click technique has been also successfully used to modify the nanocarbon materials such as carbon nanotube (CNT), graphene, and fullerene because of the effectiveness of click coupling for functionalization of nanocarbons with organic compounds and polymer chains [15–18]. Because there are present many hydroxyl groups in the surfaces of GO, the GO is very useful for attachment of alkyne or azide moieties on the GO surfaces which is necessary for GO functionalization. In addition, the graphene has the laser-induced photothermal properties according to the localized surface Plasmon resonance of graphene, depending on the states of defects, functionalization, networks of graphene, etc. [19–21]. The photothermal properties have been recently applied to polymer nanocomposites with CNTs and graphene for a variety of applications such as photothermal imaging, photothermal therapy, drug delivery, photoactuators and fiber processing. For example, the

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Plasmon enhanced photocurrent generation has been demonstrated from the click chemically modified graphene hybrids with Au nanoparticles [22]. The thin and mechanically strong nanofibers have been also achieved in the near infrared laser heated electrospinning of poly(ethylene terephthalate)/CNT nanofibers using the photothermal properties of CNTs [23].

In this study, we report synthesis of the chemically bonded stitched GO sheets obtained by click coupling and fabrication of polyurethane (PU) nanocomposites incorporating the click coupled GO sheets with enhanced mechanical and photothermal properties.

2. Experimental

2.1. Materials

Graphite was purchased from Sigma Aldrich Co. (Korea), and the GO was prepared from the graphite using an improved Hummers method [24]. 2-Chloroethyl isocyanate, sodium azide, propargylamine, N,N′-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino) pyridine (DMAP), copper bromide, sodium ascorbate, N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA), and dichloromethane (DCM) were purchased from Sigma Aldrich Co. (Korea) and were used without further purification. N,N-dimethylformamide (DMF, Duksan, Korea) was used after purification by conventional technique and stored with 4 Å type molecular sieves. All other reagents and solvents were purchased from SK Chemicals (Korea). Polyurethane (PU) (SK Chemical, R195, Korea) was used as a polymer matrix for preparation of the graphene nanocomposites.

2.2. Synthesis of 2-chloroethyl isocyanate-treated graphene oxide (Cl-GO)

GO (200 mg) with anhydrous DMF homogeneous suspension after 1 h sonication was poured into a 100 mL round-bottom flask equipped with a magnetic stirring bar. Then 2 mL of 2-chloroethyl isocyanate was added to the GO solution and the mixtures were stirred under nitrogen for 24 h to obtain Cl-GO as shown in Scheme 1 (step 1) [24]. After stirring for 24 h, the reaction mixture was filtered through a 0.2 μm PTFE membrane, washed with DCM (1 L), and dried under vacuum at 40 °C.

2.3. Synthesis of azide-moiety graphene oxide (azide-GO)

In a 100 mL round bottom flask, 1.95 g (30 mmol) of sodium azide powders was added to 200 mg of Cl-GO dissolved in 20 mL of DMF after sonication using a bath type sonicator at an ice bath for 30 min. After the sonication, the mixtures were stirred and refluxed for 24 h at 70 °C in a oil bath at constant temperature. Then the azide-GO was obtained by introducing the azide moiety on the Cl-GO via a nucleophile substitution reaction of alkyl halide. The product of azide-GO was obtained after filtration of the reacted solution (step 1, Scheme 1) [25] through a 0.2 μm PTFE membrane, washed with additional methanol (500 mL), and dried under vacuum at 40 °C.

2.4. Synthesis of alkyne-moiety graphene oxide (alkyne-GO)

In a 100 mL two-neck round-bottom flask with a nitrogen inlet, 200 mg of GO was dispersed in 15 mL of DMF and sonicated in a bath type sonicator at room temperature for 1 h. After addition of 8.61 g of DCC (41.7 mmol), 0.6 g of DMAP (4.92 mmol), and 0.3 g of propargylamine (5.46 mmol), the solution was stirred at 40 °C with continuous stirring for 24 h. The product of alkyne-GO was obtained after filtration of the reacted solution (step 2, Scheme 1) [26] through a 0.2 μm PTFE membrane, and washed several times with DMF, methanol, and distilled water, followed by drying overnight under vacuum at 40 °C.

2.5. Click coupling between azide-GO and alkyne-GO

The click chemistry reaction was used for the coupling between azide-GO and alkyne-GO (step 3, Scheme 1). Azide-GO (20 mg) and alkyne-GO (20 mg) were dispersed in 15 mL of DMF and DCM with sonication in the bath sonicator at room temperature for 10 min, respectively. 19.2 mg of copper bromide (0.134 mmol) and 34 μL of PMDETA (0.163 mmol) and 7 mg of sodium ascorbate (0.34 mmol) were dissolved in 10 mL of distilled water at room temperature for 30 min. In a 100 mL two-neck round-bottom flask equipped with a magnetic stirrer, two suspended solutions were injected into the flask at 60 °C with continuous stirring for 24 h under a nitrogen atmosphere. After completion of the reaction, the product was separated from the reaction mixture by filtration, and washed several times with DCM, DMF and distilled water, followed by drying under vacuum at room temperature.

2.6. Preparation of graphene/polyurethane nanocomposites

The graphene/polyurerthane nanocomposite films were prepared by a solvent-casting method. First, GO and GO-click-GO were dispersed in 4.77 mL of DMF at a concentration of 0.1 and 0.5 wt%, respectively by sonication using both bath- and horn-type sonicators for 1 h. After the sonication, 0.5 g of PU was added to the GO and GO-click-GO solutions, and the graphene solutions were stirred for 48 h in order to be homogeneous. Then the solutions were dried in a vacuum oven at 40 °C for 48 h to obtain the final graphene/PU films. The average thickness of the resulting nanocomposite films was 117 μm.

2.7. Measurements

Fourier transform infrared spectra (FT-IR, FT-IR 300E, Jasco, Japan) for GO, alkyne-GO, azide-GO, and GO-click-GO were recorded using KBr method. The IR spectra were scanned at resolution of 4 cm^{-1} with 100 scans for each measurement. X-ray photoelectron spectroscopy (XPS, ESCSA 2000) and field-emission scanning electron microscope energy dispersive X-ray spectroscopy (FE-SEM EDS, SUPRA 55VP, Carl Zeiss, Germany) were used to analyze the surface compositions and morphology of GO and GO-click-GO. Field-emission scanning electron microscope (FE-SEM, S-4300SE, Hitachi, Japan) was used to observe the fracture surface morphology of the nanocomposites broken under liquid nitrogen. Wide-angle X-ray diffraction (WAXD) measurements were carried out using a New D8-Advance diffractometer (Bruker-AXS) with a Cu Kα X-ray source. Raman spectroscopy was performed using a Horiba Jobin Yvon LabRam Aramis spectrometer (France) equipped with a motorized sample stage. A He–Ne laser (632.8 nm) was used as the excitation source with the beam intensity measured at the sample surface of ~1.0 mW to avoid heating. The surface morphology of GO and GO-click-GO was observed by FE-SEM (S-4300SE, Hitachi) and high resolution transmission electron microscopy (HR-TEM, JEM 2100F, JEOL, Japan). The nanostructures of spin coated samples (2000 rpm for 60 s) on silicon wafers were observed using tapping-mode atomic force microscopy (AFM) measurement. The electrical conductivity of the samples was measured by a four-probe conductivity measurement apparatus (Jandel, Model RM3-AR) at room temperature. The photothermal properties of samples were measured by exposing the samples to a near-infrared 808 nm laser at 67.5 mW/cm^2 for 4 s. The surface temperature of the samples was measured with an infrared camera (Thermovision A320M, FLIR Systems Inc.), where the temperature