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Nanodiamond nanocluster-decorated graphene oxide/epoxy nanocomposites with enhanced mechanical behavior and thermal stability

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ABSTRACT

Novel hybrid fillers composed of nanodiamond (ND) nanocluster-decorated graphene oxide (GO) were fabricated and incorporated in an epoxy matrix using a facile thermoregulatory liquid-liquid extraction method. X-ray diffraction spectroscopy, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy analyses confirmed a chemical bonding between the (3-aminopropyl)triethoxysilane-functionalized ND and (3-glycidyloxypropyl)trimethoxysilane-functionalized GO. The morphology of the hybrid filler (GN) was characterized by field-emission transmission electron microscopy. ND nanoclusters with an average diameter of 50–100 nm were uniformly grown on the GO surface. The hybrid filler provided significant enhancement of mechanical properties, such as flexural strength, flexural modulus, and fracture toughness. In particular, the epoxy composite containing 0.1 wt% of GN hybrid exhibited a stronger mechanical behavior compared to that containing 0.2 wt% of GO. As the GN loading increased, the thermal stability, the integral procedural decomposition temperature, and the activation energy increased as well. The toughening mechanism was illustrated by a microcrack theory based on the microscopic analysis of the fracture surfaces. The presence of ND nanoclusters not only hindered the aggregation of the GO sheets, but also played a crack pinning role in the polymer-matrix composites, which could significantly enhance its fracture toughness.

1. Introduction

Epoxies, with two or more active epoxy groups at the end, middle, or cyclic structure of a molecular chain, can react with various types of curing agents to form insoluble three-dimensional mesh structural polymers. Due to their high tensile modulus, good adhesive properties, chemical resistance, and excellent dimensional stability [1] [2], cured epoxy resins are commonly used in various sectors of national defense and national economy, such as paints and coatings [3], adhesives [4], composites [5], electrical systems and electronics [6] [7], and marine [8] and aerospace applications [9].

However, most of the high-performance epoxy resins exhibit an inherent brittle nature and poor crack resistance, which limits their use in mechanical equipment. The methods commonly used to improve brittleness include the incorporation of polymer [10], carbon-based materials [11] [12] [13], and nano- or micro-sized particle fillers [14] [15]. Among them, rubber-based epoxy materials are usually resulting in a reduction of the mechanical and thermal properties, while carbon-based nanofillers can significantly enhance the mechanical and dielectric properties, as well as slightly improve its thermal stability. Nanosized particles have received increasing attention in the composite area not only because of their superior reinforcement ability, but also because of their good processability at low cost, and accordingly, various functional materials have been developed. Qing et al. prepared multi-walled carbon nanotubes (MWCNTs) and carbonyl iron particles/epoxy-silicone nanocomposites and revealed that the complex permittivity of the composites increased with increasing MWCNT content, and a double resonance behavior of the complex permeability was observed as well [16]. Bestaoui et al. constructed epoxy nanocomposites based on synthetic r-zirconium phosphate layer structures and observed that the rubbery plateau modulus of

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the M-R-ZrP/epoxy nanocomposite was ~4.5 times higher than that of the M/epoxy; in addition, the tensile modulus of the M-R-ZrP/epoxy nanocomposites increased 50% compared to the reference epoxy [17]. Zhu et al. fabricated core-shell structured Fe@FeO/epoxy nanoparticles, and the results revealed that the glass transition temperature increased by 10 °C after addition of the nanoparticles; moreover, the saturation magnetization of the 20 wt% Fe@FeO/epoxy nanocomposites was ~15.8% of the pure Fe@FeO nanoparticles, and the electrical conductivity and tensile strength also improved [18].

Graphene oxide (GO), with hybridized carbon atoms in a two-dimensional honeycomb structure, has attracted increasing attention of the scientific community; accordingly, GO/epoxy nanocomposites have been extensively studied and various novel and specific functional materials have been reported [19] [20] [21]. Surprisingly, these advanced materials exhibit excellent properties, such as mechanical, dielectric, thermal stability, thermal conductivity, and smart sensing ability, due to the unique electronic, mechanical, and thermal properties of GO.

Nanodiamond (ND), fabricated by detonation techniques, have unique surface structures, superior thermal conductivity and stability, excellent mechanical and electrical properties, as well as outstanding tribological properties. The exceptional mechanical and optical properties of diamond nanoparticles, in combination with their biocompatibility, have also attracted attention recently [22]. The surface modification of ND by covalently grafting active groups and its incorporation in polymer matrices are required for several applications. Similarly to carbon nanotubes and other graphitic nanoparticles, different functional groups can be attached to the ND surface, allowing for a sophisticated surface functionalization without compromising the excellent ND properties, as already mentioned [23]. Zhai et al. incorporated low ND powder (NDP) content in an epoxy and revealed that with a NDP content of only 0.3 wt%, the Vickers hardness, tensile strength, and tensile modulus of the NDP/epoxy nanocomposites were significantly higher than those of pure epoxy [24]. Covalently bonded ND/epoxy composites showed hardness three-times higher, Young's modulus 50% higher, and creep two-times lower compared to the composites where ND were not chemically linked to the matrix [22].

Herein, we developed for the first time novel GO-ND (GN) hybrid nanofillers by covalent bonding. Specifically, GO and ND were modified with epoxy-terminated (3-glycidyloxypropyl)trimethoxysilane (GLYMO) and amine-terminated (3-aminopropyl) triethoxysilane (APTES), respectively, and subsequent bonding by epoxide-opening reaction with the amine to obtain hybrid nanofillers, GN. Their synergistic effect on the mechanical properties and thermal stabilities of the epoxy nanocomposites was investigated.

2. Experimental

2.1. Materials

The epoxy resin (diglycidyl ether of bisphenol A), which has an epoxide equivalent weight of 185–190 g eq^{-1} and a density of ~1.16 g cm^{-3} at 25 °C, was supplied by Kukdo Chemical Co., Korea. The hardener 4,4'-diaminodiphenylmethane used in this study was supplied by TCI Co., Japan. The ND, graphite flakes (GF), ammonium hydroxide, APTES, and GLYMO were purchased from Sigma-Aldrich. Anhydrous ethanol (99.9%) was supplied by Daejung Chemicals and Metals Co., Ltd., Korea. Hydrogen peroxide (30 wt% H_2O_2 solution in water) and 85% phosphoric acid (H_3PO_4) were supplied by Duksan Pure Chemicals, Korea.

2.2. Synthesis of GO and GO-GLYMO

GO was prepared using an improved Hummers' method [25]. Firstly, a concentrated mixture of H_2SO_4/H_3PO_4 (120:13.3 mL) was added to a 250 mL three-necked round-bottom flask that contained 1.0 g of GF under strong stirring in a cold-water bath. Then, 6 g of $KMnO_4$ was added slowly to the liquid mixture maintaining the temperature at ~0 °C for 4 h. The temperature was then raised to 40 °C for 12 h followed by 50 °C for 12 h. The mixture was poured in cold water and the H_2O_2 solution was added until the gas formation stopped, as the solution became bright yellow. Finally, the solution was treated according the following steps: static precipitation, discarded the supernatant, washed with acetone and deionized water, followed by infiltration through permeable membranes until the pH reached ~6. The aqueous GO suspensions were frozen in liquid N_2, and then freeze-dried using a lyophilizer (FD 8508, iLshinBioBase, Korea) at −75 °C and 0.045 mbar for 72 h to obtain low density and loosely packed GO powders.

GO (0.8 g) was charged into a 250 mL basic GLYMO-ethanol solution in a round-bottom 500 mL glass flask with a Teflon-coated magnetic stirring bar. The solution was firstly sonicated in an ultrasound bath until no particles could be observed. Then, the mixture was refluxed at 78 °C under pH 11 by adding ammonium hydroxide. After 24 h, the product was washed with ethanol and deionized water to eliminate the GLYMO excess, and then dried in an oven at 70 °C for 48 h.

2.3. Synthesis of ND-APTES

Pristine ND (0.8 g) were mixed with 250 mL of APTES-absolute ethanol in a round-bottom 500 mL flask with a Teflon-coated magnetic stirring bar. The flask was sonicated in an ultrasound bath until no ND agglomerates could be observed. Then, the mixture was refluxed at 78 °C under pH 11 by adding ammonium hydroxide. After cooling to room temperature, the mixture was centrifuged and washed with ethanol and deionized water to eliminate the APTES excess. This process was repeated several times until the pH of the supernatant reached 7. The solid was further dried at 70 °C for 12 h.

2.4. Preparation of GN

GO-GLYMO (0.4 g) and ND-APTES (0.4 g) were dispersed in 200 mL of an ethanol solution and then exfoliated by ultrasonication for 30 min. Then, the two solutions were mixed in a round-bottom 500 mL flask with a Teflon-coated magnetic stirring bar, and heated under reflux at 60 °C for 12 h. After cooling to room temperature, the sediment was collected by filtration and washed ten times with deionized water, and then dried at 80 °C in vacuum and ground to a fine powder.

2.5. Fabrication of the epoxy nanocomposites

The schematic diagram for the preparation of the epoxy/GN nanocomposites is shown in Fig. 1. The epoxy composites containing GO and GN were prepared using a standard formulation of the liquid-liquid extraction method (Fig. 1(b)): 60 g of ethanol was added to 100 g of epoxy colloid, followed by stirring at 80 °C for 10 min for the purpose of decreasing the viscosity of the epoxy. Then, the required quantity of filler was dispersed in ethanol by sonication for 30 min, followed by mixing with the above-prepared epoxy-ethanol solution under vigorous stirring for 1 h at 80 °C. After cooling in a freezer, a liquid-liquid biphasic mixture was generated, as shown in Fig. 1(b)–4. The upper phase consisted of a solution with low ethanol-epoxy concentration, which can be