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Thermal, impact and toughness behaviors of expanded graphite/graphite oxide-filled epoxy composites

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ABSTRACT

Expanded graphite (EG)/graphite oxide (GO)-filled composites were prepared and their thermal and mechanical properties were investigated. The thermal behaviors of the composites were examined by performing differential scanning calorimetry (DSC) and thermogravimetric analyzer (TGA) measurements. The mechanical properties were determined by measuring the impact strength and calculating the critical stress intensity factor (K_{IC}). The results obtained in this study indicated that the thermal stability value, which was calculated using the integral procedural decomposition temperature (IPDT), increased from 391.0 °C to 406.0 °C. The fracture toughness of the composites is improved by approximately 64% with the addition of co-carbon fillers. Notably, the co-carbon fillers contributed to improved interfacial interaction between the epoxy resin and the fillers.

1. Introduction

An increasing number of materials have been made from filler-reinforced composites [1,2]. Epoxy resins based on diglycidyl ether of bisphenol A (DGEBA) have been widely used as matrices for advanced composites, coatings, structural adhesives, and microelectronics. These composites have many useful properties such as a high tensile strength and modulus, low shrinkage, good adhesion, high heat resistance, good dimensional stability, outstanding mechanical and insulating properties, and excellent chemical corrosion resistance. Epoxy resins are key materials in polymer engineering. In particular, these materials have relatively good thermal stability, combined with a high stiffness and strength and a low creep. Among the various polymer matrices that are currently available, epoxy resins remain dominant for the development of high-performance materials because of their thermal stability, mechanical properties, and processibility [3–5].

However, cured epoxy has limited engineering applications because of its inherent brittleness, which is due to its poor resistance to crack initiation and high crosslinking density [6,7]. Accordingly, attempts have been made to improve the structural composites and physical properties of these resins by adding various nano-sized fillers to epoxy matrices. Epoxy resins are generally modified by adding liquid elastomers, thermoplastics, and inorganic particles [8–11].

In recent years, various carbon materials have emerged as potential fillers for polymer composites. Fillers composed of carbon-based materials such as carbon black, carbon nanotubes, carbon fiber, graphite nanosheets, and graphite nanoplates have displayed beneficial properties when employed in various applications. Carbon fillers can have a positive impact on the physical and chemical properties of composites [12,13]. In several studies, carbon fillers have been successfully dispersed into epoxy resins, thereby improving their fracture toughness, flame retardance, and heat resistance, and reducing the coefficient of thermal expansion [14–16].

Expanded graphite (EG) can be easily obtained by oxidizing natural graphite and inducing thermal expansion by heating for a short time. EG is a promising candidate filler for use in composites because of its low cost, low density, high thermal resistance, high electrical conductivity, high thermal conductivity, and good chemical stability from the substantial specific surface area provided by the galleries between EG nanosheets and the pores in the EG network. Therefore, EG is a more efficient filler than carbon black or graphite. EG has been used as a nanofiller in a wide range of polymer matrices, including polyetherimide, polyurethane, polypropylene, and poly(ethylene disulfide). EG-based composites

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have been investigated for their outstanding thermal properties [17,18].

Commonly, graphite is oxidized to graphite oxide (GO) and then chemically or thermally reduced to produce functionalized graphite. During the oxidation of graphite, various oxygen-containing functional groups such as epoxides, hydroxyls, ketones, and quinones are incorporated into the layers. The presence of functional groups improves the compatibility of graphite with various matrix polymers and promotes the dispersion of graphite in an epoxy, organic solvent, or water, yielding excellent mechanical and thermal properties [19–22].

Studies have been performed to investigate the thermal and mechanical properties of composites containing co-carbon fillers with different shapes, sizes, and functionalities from those of graphite. Using co-carbon fillers such as EG with carbon black or graphene nanoplatelets with carbon nanotubes may reduce the total filler content as a result of the formation of a supporting network between the two fillers. This synergistic effect leads to substantial improvements in the mechanical and thermal properties of the composite relative to those of composites with individual carbon fillers because of the double reinforcement by the co-carbon fillers [23–25].

In this work, EG and GO were employed as co-carbon fillers, and their effects on the thermal and mechanical properties of epoxy composites were investigated.

2. Experimental

2.1. Materials

Natural graphite in particle form with an average diameter of 500 μm was purchased from Sigma–Aldrich Co., Korea. The DGEBA type epoxy (YD-128), which had an epoxide equivalent weight of 185–190 g/eq and a density of about 1.16 g/cm^3 at 25 °C, was supplied by Kukdo Chemical Co., Korea. The hardener used was 4,4′-diaminodiphenylmethane (DDM), supplied by TCI Co., Japan. Nitric acid (60%) and sulfuric acid (98%) were supplied from Daejung Chemicals, Co., Korea.

2.2. Sample preparation of EGs and GOs

To produce EG, flake-type pristine graphite was added to a mixture of sulfuric acid and nitric acid (8:1 volume ratio). After reacting for 1 day, the graphite was filtered and washed with distilled water until a neutral pH was achieved, and then dried in a vacuum oven at 80 °C for 8 h. The resulting material was treated at 1000 °C for 10 s [23]. GO was prepared using the Hummers method [26]. Flake graphite was added to sulfuric acid with stirring and was then cooled in an ice bath. $KMnO_4$ was added with stirring. The reaction was allowed to proceed at 35 °C for 24 h. In the next step, distilled water was slowly added to the mixture, which was maintained at the same temperature. The reaction was terminated by the addition of hydrogen peroxide. The mixture was filtered and washed repeatedly with 10% hydrogen chloride, and then washed with acetone and dried for 24 h. The mixture was dispersed in distilled water by ultrasonication. Next, the mixture was centrifuged, and the supernatant was filtered and dried for 24 h.

2.3. Preparation of composites

Different EG:GO ratios were studied with the assumption of a maximum filler content of 1 wt%. The desired amounts of DGEBA and fillers were mixed by magnetic stirring at 80 °C for 1 h and were then sonicated for 30 min. Then, the mixture was degassed at 80 °C in a vacuum oven. Subsequently, an addition of DDM was made using mechanical mixing at 60 °C for 30 min. Then, the mixture was poured into a preheated mold. Finally, the curing steps were performed in a convection oven at 130 °C for 1 h, 150 °C for 2 h, and 170 °C for 1 h. The compositions of the EG/GO-filled epoxy composites are presented in Table 1.

2.4. Characterization and measurements

The structural properties of the EG, GO, and prepared composites were examined using X-ray diffraction (XRD, Bruker D2 PHASER). Infrared spectra were obtained using Fourier transform infrared spectroscopy (FT-IR, Jasco PS-4000). The morphologies of the EG, GO, and prepared composites were observed using a scanning electron microscope (SEM, Hitachi SU8010). The thermal stability of each composite was analyzed using a thermogravimetric analyzer (TGA, NETZSCH TG 209 F3) at a heating rate of 10 °C min^{-1} from 30 °C to 850 °C under a nitrogen atmosphere. The curing behavior of each composite was examined using differential scanning calorimetry (DSC, TA Q100) at a heating rate of 10 °C min^{-1} from 30 °C to 300 °C under a nitrogen flow of 30 ml min^{-1}. Izod impact tests were performed on notched specimens using an impact testing machine (SSAUL BESTECH, BESTIPT-320I), according to ASTM D-256. The specimen size was 5 mm × 12.7 mm × 63.5 mm. The fracture toughness values of the prepared composites were measured using single-edge-notched (SEN) specimens; the tests were performed using a universal testing machine (UTM, LLOYD, LR5K), according to ASTM E-399. The sample size was 5 mm × 10 mm × 50 mm, and the cross-head speed was 0.85 mm min^{-1}.

3. Results and discussion

The morphologies of the pristine graphite, GO, and EG are shown in Fig. 1. Multiple layers of graphite were expanded as a result of oxidation. The surface of the pristine graphite was flatter than those of the EG and GO, which exhibited pleated, flake-like morphologies. The images show the expanded, feather-like structure of the GO. Furthermore, the flake-like morphology of the graphite and its ordered structures were completely retained in the basal region of Fig. 1(b). Fig. 1(c) shows the morphology of the EG. The rapid heating of graphite at a high temperature led to expansion, which was caused by the escape of sulfuric acid that had intercalated into the graphite interlayers. Therefore, the EG developed a loose and porous structure, leading to good filler properties such as many pores of various sizes, a low specific gravity, and a larger surface area than that of natural graphite.

The XRD patterns of the EG, GO, DGEBA, and prepared composites are shown in Fig. 2. The EG and GO exhibited peaks in accord with those found in previous reports [27,28]. The interlayer distance (d_{002}) was calculated from the C (002) peak of the X-ray diffraction (XRD) pattern using the following equation (Bragg's law) [29]:

Table 1
Composition of EG/GO-filled epoxy composites.

Specimens	EG/GO-filled epoxy composites	
	EG (wt%)	GO (wt%)
DGEBA	0	0
DGEBA/EG_1	1	0
DGEBA/$EG_{0.75}$/$GO_{0.25}$	0.75	0.25
DGEBA/$EG_{0.5}$/$GO_{0.5}$	0.5	0.5
DGEBA/$EG_{0.25}$/$GO_{0.75}$	0.25	0.75
DGEBA/GO_1	0	1