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Thermal properties of epoxy resin/filler hybrid composites

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ABSTRACT

Epoxy resin/filler hybrid composites were prepared by the melt blending of diglycidylether of bisphenol-A (DGEBA), as the epoxy resin, with nano-Al_2O_3 or nano-SiC particles, as the nanoscaled fillers. The thermal properties, such as the curing behavior, thermal stability, dynamic mechanical properties, and thermal mechanical properties of the DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites were examined using a range of techniques. As a result, the DSC curve peak temperature of both composites decreased with increasing filler content. The integral procedure decomposition temperature increased from 630 °C to 853 °C for DGEBA/nano-Al_2O_3 composite and 858 °C for DGEBA/nano-SiC composite. The char yield at 800 °C increased from 14.3% to 26.2–26.6% for both composites. Both composites had a 10 °C higher glass transition temperature than the neat epoxy resin. The coefficient of thermal expansion of both composites at the glassy and rubbery regions decreased with increasing filler content.

1. Introduction

Inorganic fillers are added to the epoxy formulations to form organic–inorganic composites to improve the thermal stability, glass transition temperature, and dimensional stability of epoxy resins. Nanoscale fillers, such as nano-particles, nano-tubes, and layered silicate clays, are used widely in the preparation of epoxy composites [1–3]. Directly blending the epoxy resins and nano-particles provides a convenient route to form epoxy resin-inorganic hybrid composites [4].

Several studies have examined the preparation and thermal characterization of epoxy resins using a range of inorganic fillers. Tarrío-Saavedra et al. fabricated epoxy resin/fumed silica composites to improve the thermal stability of the epoxy resin [5]. These results suggest that the thermal stability of the epoxy resin was improved and the mass loss rate was reduced by the addition of fumed silica. Kuan et al. examined the flame retardance and thermal stability of the carbon nanotube/epoxy composites prepared using sol–gel method [6]. They concluded that the glass transition temperature (T_g) and integral procedural decomposition temperature (IPDT) were increased from 118 to 160 °C and from 890 to 1571 °C, respectively. Macan et al. investigated the thermal degradation of epoxy/silica organic/inorganic hybrid materials [7]. The resulting hybrid materials exhibited higher thermal stability, such as the temperature of the maximum degradation rate (T_{max}) and the IPDT, compared to the neat epoxy resin. Chiang et al. studied the thermal stability and degradation kinetics of novel organic/inorganic epoxy hybrid composites containing nitrogen/silicon/phosphorus [8]. The thermal stability of the hybrid composites increased with increasing content of inorganic components. Liu et al. investigated the thermal stability of epoxy/silica hybrid materials by thermogravimetric analysis (TGA) [4]. Their results suggested that the thermal stability and weight loss rates of the epoxy resins were improved by introducing nanoscale colloidal silica to form epoxy-silica nanocomposites.

In this study, epoxy resin/filler hybrid composites were prepared from diglycidylether of bisphenol-A (DGEBA), as the epoxy resin, and nano-Al_2O_3 and nano-SiC particles, as the nano-scaled fillers. The thermal properties, such as the curing behavior, thermal stability, dynamic mechanical properties, and thermal mechanical properties of the DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites were investigated by a differential scanning calorimetry (DSC), TGA, dynamic mechanical analysis (DMA), and thermal mechanical analysis (TMA).

2. Experimental

2.1. Materials

The diglycidylether of bisphenol-A (DGEBA, Kukdo Chem. of Korea) had an epoxide equivalent weight of 185–190 g/eq and a density of approximately 1.16 g/cm^3 at 25 °C. 4,4′-Diaminodiphenyl

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methane (DDM, Aldrich Chem.) was selected as a curing agent. The nano-Al_2O_3 (γ-Al_2O_3) particles were obtained from Nanjing High Technology Nano Material Co. in China. The grain size and specific surface area of the nano-Al_2O_3 particles were 20 nm and 160 m^2/g, respectively. The nano-SiC particles were supplied by Xuzhou Hongwu Nano Materials INC of China. The diameter of the nano-SiC particles was <100 nm.

2.2. Sample preparation

The weight content of the fillers was varied from 5 to 15 wt%. The desired amounts of DGEBA and filler were mixed with a magnetic stirring bar at 80 °C for 1 h and treated ultrasonically for 30 min. Subsequently, DDM was added to the mixture. The bubble-free mixture was poured into a preheated mold, which had previously been sprayed with a mold release agent. Initial cure temperature and final cure temperature of DGEBA/DDM system was 102.5 and 224.6 °C, respectively. The curing cycle used in this study was determined according to the curing characteristics. Curing was performed at 110 °C for 1 h, at 140 °C for 2 h, and at 170 °C for 1 h in a convection oven.

2.3. Characterization and measurements

The cure behavior of DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC samples was examined by a DSC (NETZSCH, DSC 200 F3) at a heating rate of 10 °C/min from 30 to 300 °C under a nitrogen flow of 30 ml/min.

Dispersion state of nano-particles in epoxy matrix was investigated using a Field Emissio-Transmission Electron Microscope (FE-TEM, JEM2100/JEOL) with an accelerating voltage of 200 kV.

The thermal stability of the DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites was analyzed with TGA (NETZSCH TG 209 F3) at a heating rate of 10 °C/min from 30 to 850 °C under a nitrogen atmosphere.

The dynamic mechanical properties of the composites were determined by DMA (RDS-II, Rhemetrics Co.) at a frequency of 1 Hz, temperature range from 35 to 250 °C, and heating rate of 5 °C/min. The specimen dimensions were 2 mm × 12 mm × 35 mm.

The coefficient of thermal expansion (CTE) of the composites was determined by TMA (RDS-II, Rheometrics Co.) with an applied a force of 0.05 N at a heating rate of 5 °C/min under a nitrogen atmosphere. The CTE was calculated using the following equation:

$$\alpha = \frac{1}{L_0}\frac{\Delta L}{\Delta T} \quad (1)$$

where L_0 is the initial length, ΔL is the change in length, and ΔT is the temperature range.

3. Results and discussion

3.1. Curing behavior

The effect of fillers, nano-Al_2O_3 and nano-SiC particles, on the curing behavior of the DGEBA epoxy resin cured with DDM was examined by DSC, and the dynamic DSC thermograms are shown in Fig. 1. The peak maximum temperature (T_p) and reaction enthalpy (ΔH) were calculated from the thermograms, and the results are summarized in Table 1. The T_p of DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites shifted towards a lower temperature with increasing filler content. The T_p decreased from 163.4 to 147.1 °C for the DGEBA/nano-Al_2O_3 composites and 158.5 °C for the DGEBA/nano-SiC composites. These results suggest that the nano-Al_2O_3 and nano-SiC particles have a catalytic effect on the curing

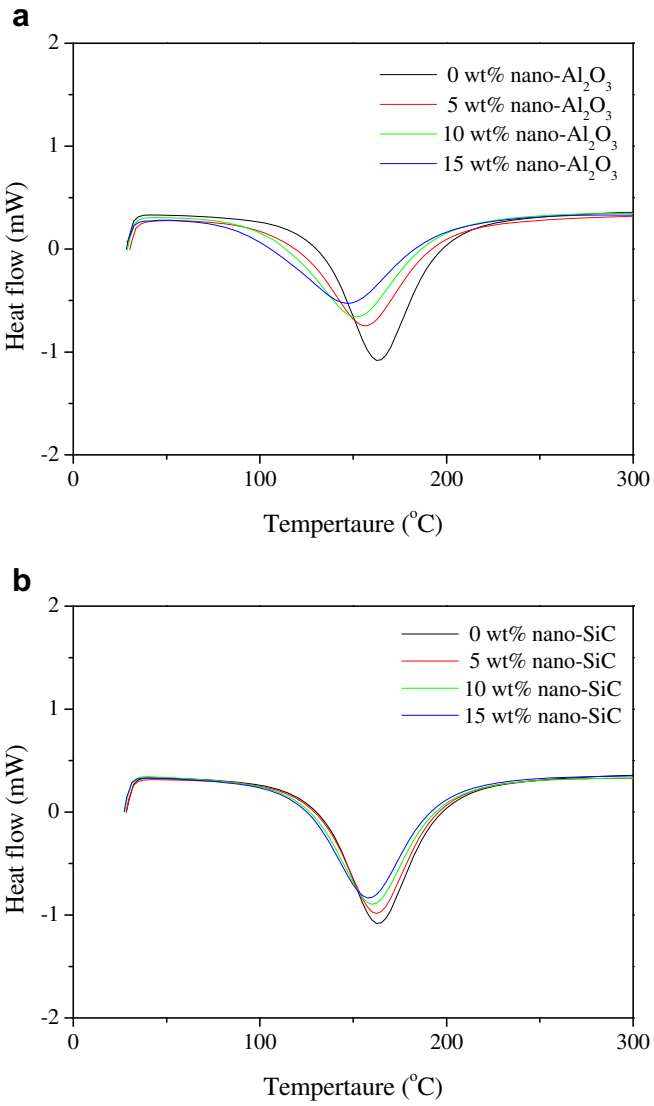

Fig. 1. DSC thermograms of (a) DGEBA/nano-Al_2O_3 and (b) DGEBA/nano-SiC composites.

reactions of the epoxy resins [9,10]. The T_p of DGEBA/nano-Al_2O_3 composites is lower than that of the DGEBA/nano-SiC composites under similar conditions, which due to acceleration of the amine–epoxide reaction by traces of hydroxyl groups in the nano-Al_2O_3 surfaces.

As shown in Table 1, the ΔH based on epoxy of the DGEBA/nano-Al_2O_3 composites was lower than that of the DGEBA/DDM sample and the ΔH based on epoxy of the DGEBA/nano-SiC composites was

Table 1
Peak maximum temperature (T_p) and reaction enthalpy (ΔH) of DGEBA/nano-Al_2O_3 and DGEBA/nano-SiC composites.

Al_2O_3 content (wt%)	SiC content (wt%)	T_p (°C)	ΔH (J/g-sample)	ΔH (J/g-epoxy)
0	0	163.4	406.7	549.6
5	0	156.5	365.6	529.9
10	0	151.8	346.5	541.4
15	0	147.1	316.0	535.6
0	5	162.5	387.0	560.9
0	10	160.5	374.0	584.4
0	15	158.5	363.7	616.4