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Pitch coating of SiC and its effects on the thermal stability and oxidation resistance of SiC/epoxy composites

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ABSTRACT

The effects of surface treatment and carbonized pitch (CP) coating on the silicon carbide (SiC) in a SiC epoxy composite were investigated in this study, with a focus on the thermal stability and oxidation resistance of the composites. The thermal stability and oxidation resistance properties of the composites were affected by this CP coating. The SiC pitch coating improved the thermal stability and oxidation resistance of the epoxy composite, and the CP coated-SiC filler improved the thermal stability of the epoxy composites over that of the pure SiC filler. In addition, the surface treatment increased the thermal stability and oxidation resistance due to the interaction at the surface between the SiC and the CP. CP-coated acidic surface treated-SiC (CP/aSiC) composites featured improved oxidation resistance and thermal stability compared to the CP coated-SiC (CP/SiC) composites.

1. Introduction

Epoxy resins are used in a wide variety of applications such as coatings, electronic materials, adhesives, and matrices for ceramic-filler-reinforced composites. The versatility of epoxy resins arises from a number of characteristics including their flexibility, hardness, high adhesion strength, good heat resistance, and high electrical resistance [1–3]. However, cured epoxy resins are inherently brittle due to the high cross-linking density, which hinders the use of epoxy resins in many engineering applications [4]. Epoxy resins have been previously modified with liquid elastomers, thermoplastics, and inorganic fillers to overcome this issue [5]. To date, the predominant strategy for toughening epoxy resins is the incorporation of a secondary phase, such as fibers [6], clay [7], carbon materials such as fibers, carbon nanotubes (CNTs), and graphene [8], or inorganic fillers [9], into the epoxy matrix.

In particular, carbon materials and inorganic fillers have been previously used to improve the thermal stability, glass transition, and oxidation resistance of epoxy resins. Several studies have examined the use of a number of different carbon materials (such as CNTs and graphene) and inorganic fillers to improve these aforementioned properties. Poh et al. [10] investigated the dielectric properties of epoxy composites containing multi-walled CNTs (MWCNTs), with their results showing that loading MWCNTs increased the dielectric properties of the composite system. Shiu and Tsai [11] studied the thermal and mechanical properties of graphene/epoxy nanocomposites using molecular dynamics (MD) simulations. In the case of inorganic fillers, Amaro et al. [12] presented experimental results on the mechanical properties of epoxy resin composites reinforced with alumina nanoparticles. Wu et al. [13] studied epoxy composites containing high amounts of Al_2O_3 at various temperatures, and concluded that Al_2O_3 at any concentration improved the thermal stability of the Al_2O_3/epoxy composites, with greater improvements obtained as the Al_2O_3 contents were increased. These results demonstrate that inorganic fillers can play a role as epoxy reinforcing agents. SiCs can also play an important role in epoxy reinforcement in regards to its thermal and physical properties. Vijayan et al. [14] investigated the mechanical and thermal properties of epoxy/silicon carbide (SiC)–nanofiber composites, which showed that the mechanical and thermal properties of the composites were improved by adding the SiC nanofibers. Park et al. [15] fabricated carbon fiber (CF)/SiC/epoxy composites with improved thermal and physical properties by altering the surface properties of the SiC with electron acceptor–donor modifications. They reported that the electron–acceptor-treated SiC had a higher acidic value and a greater polar component in its surface free energy than both the untreated SiC and electron–donor-

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treated SiC. This indicates that the electron acceptor–donor interactions between the SiC and epoxy matrix can enhance the heat resistance and physical properties of such composites.

Coal-tar pitch is a thick black liquid that is left over from the distillation of coal tar. It is commonly used as a base for coatings and paint and as a binder in asphalt products. Both coal tar and coal-tar pitch contain numerous chemical compounds, including carcinogens such as benzene. Coal-tar pitch has recently taken on a role as a coating and binder in electrochemical, ceramic, and polymer fields. Bhatia [16] have already investigated the physical properties of pitch coated ceramic composites, and found that composites made from uncoated as well as pitch-coated green coke exhibited favorable physical properties.

In this study, the effects of surface treatment and CP coating on the SiC in a SiC epoxy composite were investigated, with a focus on the thermal stability and oxidation resistance of the composites. The changes of thermal stability and oxidation resistance properties due to the effects of the CP coating were determined. In addition, the effects of surface acid-treatment on the thermal stability and oxidation resistance properties of epoxy composites were investigated compared to untreated fillers.

2. Experimental methods

2.1. Materials

SiC powders were pulverized by freezer milling (Spex 6, SPEX Certi Prep Co.). Epoxy resin (diglycidyl ether of bisphenol A; DGEBA) was purchased from Kukdo Chemical Co. The curing agent 4,4′-diaminodiphenylmethane (DDM) was added during the fabrication process. The pitch was provided by GS Caltax Co., Ltd. Quinoline was used as the solvent for mixing the CP with the SiC powders.

2.2. Acidic surface treatment

The SiC powders were treated with a mixture of sulfuric and nitric acid (3:1 v/v). The acid-treated SiC (aSiC) powder was washed with water until a pH of 7.0 was reached, and the washed samples were then filtered and dried at 80 °C.

2.3. Preparation of CP/SiC

The coating solution was prepared by mixing the pitch and quinoline ata 1:10 mass ratio. The SiC and aSiC powders were coated by stirring them in a coating solution for 2 h, and the CP-coated powders were then dried in a vacuum oven at 70 °C for 12 h. After drying, the CP-coated powders were treated in a N_2-purged furnace at 800 °C for 5 min. The resulting CP/SiC powder and CP-coated, acid-treated, SiC powder (CP/aSiC) were subsequently washed in distilled water to remove any impurities.

2.4. Preparation of the SiC-loaded epoxies

The SiC/epoxy composites were prepared using a simple solution mixing-evaporation method. Briefly, 1, 3, 5, or 7 parts of SiC per hundred resin (phr) were mixed with 40 g of DGEBA in a simple solution mixing-evaporation setup (Planetary Centrifugal Mixer, ARE-310, THINKY Inc., USA) for 30 min. After mixing, 17 phr of DDM was added to the SiC/epoxy mixtures and stirred for 30 min. The mixtures were subsequently degassed for 30 min to remove any bubbles, and then allowed to cure at 120 °C for 2 h. Post-curing was performed at 150 °C for 2 h in an oven. The CP/SiC and CP/aSiC composites were fabricated in a similar manner.

2.5. Characterization and measurements

The morphology of the CP/SiC composites was determined using scanning electron microscopy (SEM, High Resolution Scanning Electron Microscope, SU 8010, Hitachi, Ltd., Japan), and the surface composition was determined using energy-dispersive spectroscopy (EDS). The acid and base values of the CP, aSiC, and SiC were determined with Boehm titrations [14], in which 1 g of either the CP, aSiC, or SiC was placed in 100 mL of a 0.1 M sodium hydroxide (NaOH) solution. The flasks were sealed and shaken for 24 h, after which 20 mL of each filtrate was titrated against a 0.1 M solution of hydrochloric acid (HCl). The number of acidic sites on the C-based surfaces was calculated from the volume of NaOH required to fully react with the C-based materials. The surface basicity was determined with a similar process. The thermal stability and oxidation resistance were analyzed by thermogravimetric analysis (TGA) at a heating rate of 10 °C/min under N_2 and air atmospheres.

3. Results and discussion

3.1. Surface properties

The total acidity of the SiC surfaces was determined according to the Boehm titration method [17,18]. Table 1 shows the acid–base values of the SiC samples before and after acidic surface treatment. As expected, the acid value of the aSiC is higher than that of the untreated SiC. The acid value of the untreated SiC is 20 meq/g (here, ‘meq’ represents a unit, which is commonly used in chemistry, that indicates the relative amount of a substance; 1 meq = 0.001 equivalent weights). When SiC is treated with H_2SO_4 to form aSiC, the acid value increases to 80 meq/g, indicating that the number of surface functional groups has significantly increased because of the H_2SO_4 treatment [15]. Thus, H_2SO_4 treatment used to fabricate the aSiC results in good interactions at the interface with the CP coating, which has a relatively high base value. These results indicate that the sample surfaces were successfully coated [17].

Fig. 1 shows representative SEM and EDS images of the SiC, CP/SiC, and CP/aSiC samples. The SiC sample exhibits a clean surface in Fig. 1(a) and (a-1). The SEM images of the CP/SiC sample (Fig. 1(b) and (b-1)) show well-coated SiC particles. These interactions were induced by the carbonization of the pitch under N_2 at 800 °C for 5 min. The SEM images in Fig. 1(b) and (b-1) also indicate that the CP/SiC particles are uniformly surrounded by aCP coating. In addition, the surface-treated CP/aSiC particles (Fig. 1(c) and (c-1)) have clean surfaces that are mostly covered by CP. This demonstrates that the acidic surface treatment aids the production of an even CP coating on the SiC particles. The EDS results show elemental compositions of the SiC and CP/SiC particles in Fig. 1(a-2) and (b-2), respectively. As expected, Fig. 1(a-2) shows that the surface of the SiC particles is composed of Si and C. On the other hand, both Fig. 1(b-2) and (c-2) indicate the presence of both SiC and CP. The EDS data of the CP/aSiC sample also indicates the presence of O-containing functional groups (Table 2). This evidence suggests that the aSiC particles were successfully coated in CP.

Table 1
Acid–base values of the SiC, aSiC, and CP.

Samples	Acid value [meq g^{-1}]	Base value [meq g^{-1}]
SiC	20	120
aSiC	80	10
CP	140	350