Preparation and thermal properties of polyacrylonitrile-based carbon fiber–silicon carbide core–shell hybrid

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ABSTRACT

A polyacrylonitrile (PAN)-based carbon fiber–silicon carbide core–shell hybrid (SiC/PAN-CF) was prepared by carbothermal reduction of SiO_2/PAN-CF, which was obtained by dip coating a SiO_2 sol on the surface of PAN-CF. The surface of the PAN-CF was uniformly covered with the SiC, and the decomposition temperature of SiC/PAN-CF was higher than that of the uncoated PAN-CF. In addition, the thermal conductivity of epoxy composites consisting of PAN-CF or SiC/PAN-CF was measured using a laser flash method. At a 80 wt% filler loading, the thermal conductivity of SiC/PAN-CF-epoxy composite was found to be 0.750 W/mK, which is 2 times higher than that of the PAN-CF-epoxy composite and approximately 3.5 times greater than that of unmodified epoxy resin. Furthermore, the thermal conductivity of SiC/PAN-CF-epoxy composite increased with increasing carbothermal reduction time. This increased thermal conductivity is due to improving the specific surface area and wettability with epoxy matrix, thus resulting in an improved the interfacial adhesion with epoxy matrix.

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1. Introduction

The generation of waste heat is a significant problem in that it reduces the lifespans of devices such as computers and cellular phones. Therefore, there is a large demand for improved means of efficient heat dissipation. Previously, both metal and ceramic materials with high heat dissipation capabilities have been used for this purpose, but these tend to suffer from the high density of metal materials, low processability, and high processing costs. In order to overcome these drawbacks, many studies have investigated polymer composites that incorporate fillers with a high thermal conductivity, including metals such as copper [1] and nickel [2]; carbon-based materials [3–5] such as carbon nanotubes (CNTs) and carbon fiber (CF); and ceramic materials such as boron nitride (BN) [6], silicon carbide (SiC) [7], and aluminum nitride (AlN) [8].

CF is one of the main reinforcements used in composite materials because of its good chemical, thermal, and mechanical properties. The major drawback to the use of CF is its low oxidation resistance. Once the temperature is above 400 °C, CF reacts with oxygen and rapidly burns away. The actual reactivity depends on the CF surface properties, but the oxidation rate always increases very quickly above 500 °C [9,10]. This drawback could be overcome by protecting the carbon with a ceramic matrix that acts as a diffusion barrier between oxygen and the carbon surface [11].

SiC has long been known for its many superior properties, such as its high hardness and strength, excellent resistance to oxidation and corrosion, low coefficient of thermal expansion, and good heat-transfer capabilities [12]. The methods used to produce SiC can be roughly classified into two categories: carbothermal reduction of silica and pyrolysis of silane compounds. The carbothermal reduction technique is simple and easy to carry out, and the coatings prepared are generally well compatible with CF.

In this study, we attempted to coat SiC on CF to prepare CF–SiC core–shell hybrids by carbothermal reduction of SiO_2. Furthermore, the thermal conductivity of the epoxy composites was investigated and thermogravimetric analysis (TGA) of CF or SiC/CF was performed, and the effect of the carbothermal reduction time of SiO_2 was studied.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN)-based CF (UTS50 F22 12K 800TEX, Toho Tenax Co.) with a diameter of about 7 μm was used in this work. A SiO_2 sol (SS-30OPAC) with a particle size of about 20 nm was supplied by S-Chemtech and used as a precursor to form a SiC layer

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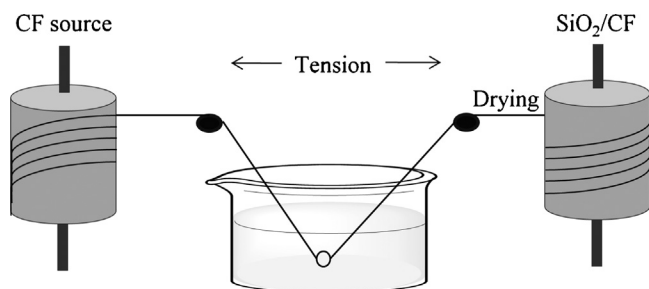Fig. 1. Schematic representation of the coating device.

Fig. 3. Heating process for fabrication of the SiC/PAN-CF hybrid filler.

on the CF. The matrix used to prepare CF-epoxy composite or SiC/CF composite was a bisphenol-A epoxy resin (YD-128) combined with a curing agent (G-A0635), both of which were supplied by Kukdo Chemical Co. The resin and curing agent were mixed at a weight ratio of 2:1 and then combined with an acetone solvent to produce a binder containing 50% solids by weight.

2.2. Preparation of SiC/PAN-CF hybrid

Before the dip coating, the surface of the commercial CF was desized by heat treatment at 950 °C under argon (95%) for 15 h. The CF was impregnated with the silica sol using the dipping device schematically represented in Fig. 1. The impregnated fibers were wound on a mandrel and kept there at room temperature for 30 min. A densified silica layer was fabricated first by heat treatment under argon up to 1000 °C for 30 min. Second, the impregnated CF was held at 1450 °C for 1, 3, or 5 h under an argon flow. The preparation procedure used to fabricate the SiC/PAN-CF hybrid filler is illustrated in Figs. 2 and 3.

2.3. Preparation of epoxy composites

An epoxy composite with PAN-CF or SiC/PAN-CF was prepared in order to study the effect of SiC coating. PAN-CF and SiC/PAN-CF was chopped in about 6 mm. The prepared PAN-CF or SiC/PAN-CF was dispersed in an epoxy resin, and the mixture was heated at 90 °C in order to completely remove the solvent. The composites were then poured into a mold, pressed at 110 °C for 1 h, and cooled to room temperature.
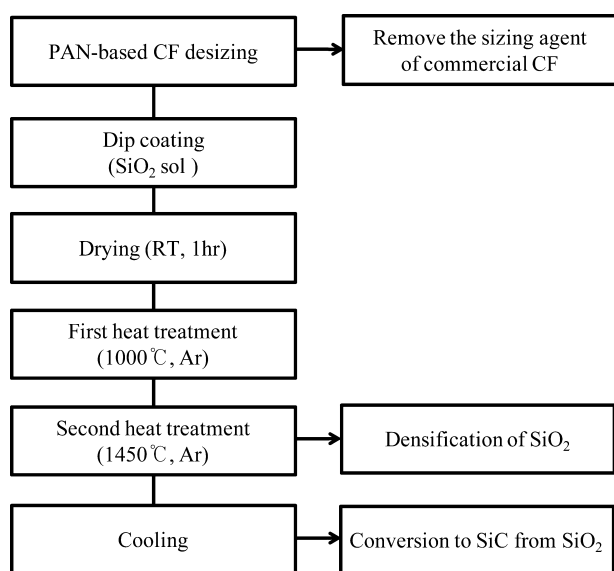

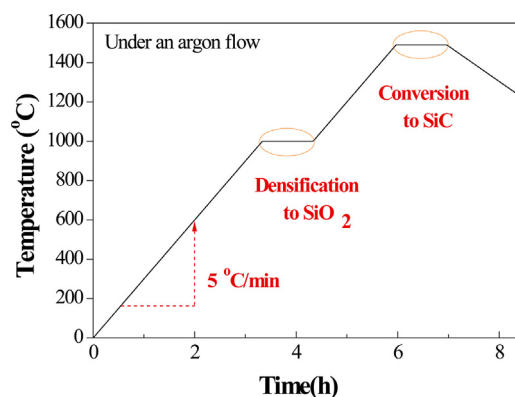Fig. 2. Fabrication process for SiC/PAN-based CF hybrid filler.

2.4. Analysis

The crystallographic phases present in the SiC-coated CF were identified by X-ray diffraction (XRD, D5005, Siemens). Scanning electron microscopy (SEM, SM300, Topcon) was used to examine the surface morphology and to measure the coating thickness of the coated fibers and the coating layer after removal of PAN-CF. Energy dispersive spectroscopy (EDS) was used to investigate the coated carbon fibers to prove that the SiC or SiOC coatings existed on the surface of the PAN-CF.

The thermal oxidation resistance of the uncoated and coated fibers was investigated using thermogravimetric analysis (TGA/DSC-1, Mettler Toledo) under an air atmosphere at a rate of 10 °C/min from 25 °C to 1000 °C.

The thermal diffusivity and heat capacity of the composites was measured by laser flash analysis (LFA-427 nanoflash apparatus, NETSZCH) at room temperature. The samples were prepared in disc-shaped forms with diameters of 12.6 mm and thicknesses of 1.5 mm for measuring the through-plane thermal conductivity and were coated with graphite to enhance the absorbance of the flash energy during LFA. Then, the thermal conductivity (k) was calculated with Eq. (1):

$$k = \alpha \rho C_P \tag{1}$$

where α, ρ, and C_P are the thermal diffusivity, density, and heat capacity of the specimen, respectively. The densities of the composites were measured by apparent density.

The contact angles were measured using a Sigma700 tensiometer (KSV Instruments Ltd.). In this technique, the wettability of the CF is determined using the wicking method, and the contact angle is then calculated using Washburn's equation (Eq. (2)):

$$\frac{m^2}{t} = \frac{c \times \rho^2 \times \gamma_L \times \cos\theta}{\eta} \tag{2}$$

where m is the weight of the penetrating liquid, t is the flow time, c is the packing factor, ρ is the density of the measuring liquid, and γ_L and η are the liquid surface tension and viscosity, respectively. The test wetting liquids used for the contact angle measurements were n-hexane and deionized water. The properties of the wetting liquids are shown in Table 1.

Table 1
Characteristics of wetting liquids.

Liquid	γ_L^L (mJ/m^2)	γ_L^{SP} (mJ/m^2)	γ_L (mJ/m^2)	η (mPa/s)	ρ (g/cm^3)
n-Hexane	18.4	0	18.4	0.33	0.661
Water	21.87	51	72.8	1	0.998