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Boride ceramics covalent functionalization and its effect on the thermal conductivity of epoxy composites

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HIGHLIGHTS

- The surfaces of ZrB_2/Al_2O_3 were functionalized by silane coupling agents.
- The thermal conductivity (TC) of modified epoxy composites is improved significantly.
- The FEM values of TC are in reasonable agreement with the experimental values.

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ABSTRACT

Zirconium diboride/aluminium oxide (ZrB_2/Al_2O_3) composite particles were functionalized with epoxide functionalized γ-glycidoxypropyltrimethoxysilane by the covalent bonding approach to improve the interfacial compatibility of composite particles in epoxy matrix. The composites of epoxy resin filled with functionalized ZrB_2/Al_2O_3 were prepared by in situ bulk condensation polymerization of bisphenol A and epichlorohydrin in the presence of ZrB_2/Al_2O_3. The heat-conducting properties of composites were investigated by the finite element method (FEM) and the thermal conductivity test. The finite-element program ANSYS was used for this numerical analysis, and three-dimensional spheres-in-cube lattice array models were built to simulate the microstructure of composite materials for different filler contents. The thermal conductivity of composites was determined by laser flash method (LFA447 Nanoflash), using the measured heat capacity and thermal diffusivity, with separately entered density data. The results show that the effective chemical bonds are formed between ZrB_2/Al_2O_3 and γ-glycidoxypropyltrimethoxysilane after the surface functionalization. The interfacial compatibility and bonding of modified particles with the epoxy matrix are improved. The thermal conductivities of functionalized composites with 3 vol% and 5 vol% loading are increased by 8.3% and 12.5% relative to the unmodified composites, respectively. Comparison of experimental values and calculated values of the thermal conductivity, the average relative differences are under 5%. The predictive values of thermal conductivity of epoxy composites are in reasonable agreement with the experimental values.

1. Introduction

Epoxy resin has been widely applied in the fields of engineering materials and encapsulation of electronic devices due to its outstanding mechanical performances and chemical resistance. However, the heat which is generated from the friction in engineering materials and the temperature rise caused by the working of electronic devices shorten the service life of epoxy resin. The incorporations of inorganic fillers with high thermal conductivity into the epoxy resin have been proved to be an effective method to improve the thermal performances of epoxy resin. The dispersion of inorganic particles in polymer matrix has significant effects on the properties of its filling polymer composites [1–3]. The good dispersibility of particles is quite effective to improve the performance of its filling polymer matrix, including their thermal properties [4]. In order to realize better dispersion of inorganic particles in epoxy matrix, the surface organic functional modification of inorganic particles is an effective approach. In more recent studies, some works have been reported on the improvement of dispersion

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stability of inorganic particles, such as boron nitride, aluminum nitride, silica, aluminum oxide, silicon carbide, and silicon nitride [5–11], in epoxy resins by treating the particle surfaces with silane coupling agents, which would significantly increase the thermal properties of composites. However, much less work has been done in zirconium diboride (ZrB_2) filled polymer composites. ZrB_2 is one of the most important boride ceramic materials. The crystalline structure of ZrB_2 is hexagonal and zirconium and boron atoms array in 2-D net structure, respectively. Layers of boron atoms separate layers of zirconium atoms equably. Zirconium and boron atoms combine by ionic bonding, and boron atoms combine each other by covalent bonding. This structure determines its high hardness, high melting point and good heat conduction performance [12]. In some previous reports, ZrB_2 reinforcements showed great thermal properties, especially thermal conductivity, in ceramic matrix composites (CMCs) [13–15], thus ZrB_2 seems a potential reinforcement material in the improvement of effective thermal conductivity of composites. Also, the addition of ZrB_2 fillers to epoxy resin matrix is expected to present higher thermal conductivity than that of other inorganic particulate fillers. In fact, our previous research has demonstrated that the effective thermal conductivities of epoxy composites can be improved greatly due to the addition of ZrB_2 particles into epoxy matrix, and concluded that the dispersion of ZrB_2 particles in epoxy matrix has an important influence on the thermal conductivity of composite materials [16]. Obviously, the problem of poor compatibility of ZrB_2 particles with the epoxy matrix is also the same suffered as other inorganic ceramic particles in the epoxy resin. It is very necessary to introduce the organic functional groups onto the surfaces of ZrB_2 particles for improving the compatibility and dispersion of ZrB_2 particles in the epoxy matrix. However, it is very difficult for the surface organic functional modification of ZrB_2 particles because of the lack of active groups which could react with the organic surfactants on the surfaces of ZrB_2 particles. Thus, in order to realize the organic functionalization of the surfaces of ZrB_2 particles, the introduction of the oxide ceramic particles such as Al_2O_3 particles into ZrB_2 particles to form ZrB_2/Al_2O_3 composite particles is an available means. In our previous work, ZrB_2/Al_2O_3 composite particles prepared by Self-propagating high-temperature synthesis (SHS) method have good interfacial bonding and present coherent or semi-coherent interface resulted from the crystal nucleation and growth of Al_2O_3 on the surfaces of ZrB_2 particles [17]. The literature [18] reported also on sintering behavior of the ZrB_2/Al_2O_3 composite particles and pointed out that the grain-boundary between the ZrB_2–Al_2O_3 grains clearly presented the inter-diffusion of alumina and zirconium diboride into each other and formed a complex boride or oxyboride of Zr, Al. These all imply that the surface organic functional modification of ZrB_2/Al_2O_3 composite particles can be completed and the compatibility and dispersion stability of modified ZrB_2/Al_2O_3 composite particles in epoxy matrix can be improved through the organic functional modification of Al_2O_3 particles surfaces with active groups which could react with organic coupling agent or surfactant [19] due to good interfacial bonding between ZrB_2 particles and Al_2O_3 particles. There are not many reports on the study of the effect of surface organic modification of composite particles on the thermal conductivity performance of filling composites. As mentioned in the literature [7], introducing an aminosilane to the surfaces of AlN/BN composite particles can minimize effectively the thermal resistance at the particle surfaces and optimize the contact area and thermal conducting path of the particles with the epoxy matrix and obtain high thermal properties of the composites due to good compatibility and interfacial adhesion between the composite particles and matrix polymer. Xu et al. [20] also believed that the surface treatment of AlN/BN composite particles is useful for increasing the thermal conductivity of AlN/BN particles filling epoxy matrix composites due to the decrease in thermal contact resistance at the filler–matrix interface. The literature [21] researched the thermal conductivity on the surface untreated Al_2O_3/AlN composite particles filling epoxy composites, indicating that a high thermal resistance existed in the composite interface due to poor interfacial compatibility of surface unmodified Al_2O_3/AlN with epoxy matrix. It can be further indicated that the surface organic modification of composite particles is very important for the improvement of effective thermal conductivity of composite particles filling polymer composites system.

The researches on the thermal conductivity performance of inorganic fillers filling polymer composites using numerical analysis method have been conducted [22,23]. The effective thermal conductivity of micro-sized pine wood particles filling epoxy composites was investigated by ANSYS and experimental method and showed that the values obtained using finite element analysis were found to be in reasonable agreement with the experimental values [24]. Alok Agrawal and Alok Satapathy [25] reinforced also epoxy resin with 0–15 vol% AlN and analyzed thermal conductivity by experiments and Maxwell et al.'s numerical models. There are few reports, however, on discussing the effect of the surface organic functionalization of ZrB_2/Al_2O_3 composite particles on the thermal conductivity of filling composites using numerical analysis method. The numerical analysis shows good efficiency in the predictions of composites properties. Moreover, in the field of non-linear heterogeneous composites, the finite element analysis is demonstrated to be in accordance with experimental results. Thus, in this research, we intend to explore the effects of the surface organic functionalization of ZrB_2/Al_2O_3 composite particles with epoxide functionalized γ-glycidoxypropyltrimethoxysilane on the thermal conductivities of epoxy composites. The thermal conductivity of epoxy composites is investigated by the experimental and numerical methods. The mechanism of functionalized ZrB_2/Al_2O_3 composite particles enhancing thermal properties of epoxy composites is discussed by the comparison of experimental results and simulated data.

2. Experimental

2.1. Components and physical properties of raw materials

Zirconium oxide (99% pure, <5 μm), aluminum powder (99.9% pure, <30 nm) and boron oxide (99% pure, <5 μm) were purchased from the Aladdin Industrial Corporation, China. γ-glycidoxypropyltrimethoxysilane with purity of 98% supplied by Sinopharm Chemical Reagent Co., Ltd. China was used for silane functionalization of ZrB_2/Al_2O_3. The polymeric matrix is epoxy resin, synthesized from BPA (bisphenol A, >99.0%, white crystal, Sinopharm Chemical Reagent Co. Ltd), and epichlorohydrin (>99.0%, colorless transparent oily liquid, Sinopharm Chemical Reagent). An amine hardener, triethylenetetramine (TETA), served as curing agents (Sinopharm Chemical Reagent Co., Ltd. China). Chemical structures of epoxy and silane coupling agent are shown in Fig. 1.

2.2. Self-propagating high-temperature chemical synthesis of ZrB_2/Al_2O_3 composite particles

Powdery amorphous boron oxide, Zirconium oxide and reducing agent aluminum were used as reactants for the synthesis. The mixture was prepared as per stoichiometry of reaction as follows:

$$3ZrO_2 + 3B_2O_3 + 10Al \rightarrow 3ZrB_2 + 5Al_2O_3 \quad (1)$$