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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:

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

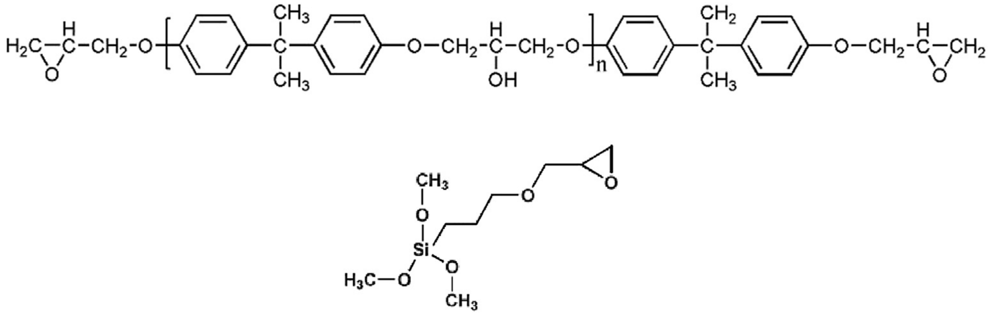

Fig. 1. Chemical structures of diglycidyl ether of bisphenol A and γ-glycidoxypropyltrimethoxysilane.

The detailed experimental procedure and reaction mechanism are available in our previous publication [17]. The X-ray diffraction (XRD) pattern of the synthesized powders is shown in Fig. 2. As shown, the synthesized powders are composed of two phases α-Al_2O_3 and ZrB_2 with hexagonal structure.

After the reaction, the synthesized products were treated by the ball-milling to fine powders. In this study, continuous grinding was performed in a high-energy planetary ball mill (PMQ, DROIDE, China) with a powder to ball weight ratio of 1/10. The grinding tools are made of zirconia (jar ≈ 50 cm^3 and ten balls, ϕ ≈ 10 mm). The powders and balls were sealed in the zirconia jars with acetone at room temperature. The zirconia jars were fixed and run at 600 rpm for 2 h. After the milling, the powders were dried at 80 °C, prepared for functionalization.

2.3. Functionalization of ZrB_2/Al_2O_3 composite particles

The γ-glycidoxypropyltrimethoxysilane (5 g) was added in an ethanol-aqueous solution prepared by the volume ratio of ethanol: water = 1:9 (250 ml). The solution was stirred for 5 min. Then the ZrB_2/Al_2O_3 composites dried at 100 °C for 1 h (50 g) were dispersed in above solution with a magnetic stirrer for 3 h, and ultrasonic process for 10 min (Sonicator: KQ5200DE Kun-Shan Instruments, China, frequency: 40 kHz). The temperature of the functionalization of composite particles was controlled at 50 °C. After the reaction, the powders were washed by acetone and dried in a vacuum oven at 80 °C for 1 h.

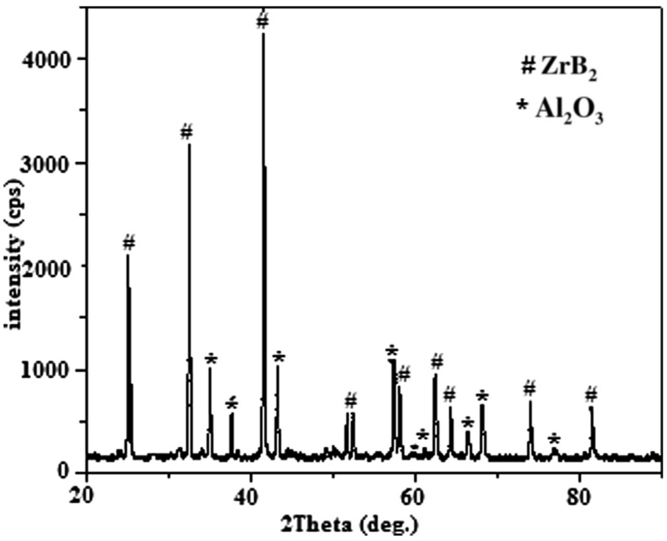

Fig. 2. XRD pattern of the synthesized powders.

2.4. Epoxy composites processing

Bisphenol A was solved in NaOH solution (about 0.3 mol/L OH^-) at 70 °C, and ZrB_2/Al_2O_3 (preprocessed by ultrasound for 30 min) particles were introduced into the solution. The temperature of the solution was reduced to 50 °C after ZrB_2 particles dispersing evenly, and added epichlorohydrin by the droplets. The reaction product was poured into the molds after the temperature of solution being raised to 90 °C for 2 h. Simethicone was used in each molds and the molds were heated over 150 °C until no solvent left. The epoxy composite mixture was mixed with 2 phr (parts per hundred resins) of curing agent (PAA). The composites were degassed in a vacuum oven at room temperature until most of entrapped bubbles were removed completely. And then, the mixtures were cured for 12 h at 50 °C. The ZrB_2/Al_2O_3 composite fillers were added in different percentages: 1 vol%, 3 vol%, and 5 vol% with regard to the volume of epoxy resin.

2.5. Materials analysis

Fourier Transform Infrared (FT-IR) measurements were performed on Bruker Vertex 70 FT-IR Spectrometer to identify surface functional groups of modified ZrB_2/Al_2O_3 composite particles. X-ray photoelectron spectroscopy (XPS) of the modified ZrB_2/Al_2O_3 composite particles were collected by 5000c ESCA produced by PHI company, America. The synthesized powders were characterized with a Philips X-ray Diffractometer (XRD, Holland). Scanning electron microscopy (SEM, PHILIPS XL30FEG) and transmission electron microscopy (TEM, JEM-2100, Japan) were used to observe the dispersion of ceramic particles and the microstructure of composites. The specimens (about 60 nm in thickness) for TEM observation were trimmed using a microtome machine with a diamond knife. The thermal conductive coefficients (W/m·K) of epoxy composites can be computed from the values of density (g/cm^3), thermal diffusion coefficient (mm^2/s) and specific heat capacity (J/g·K). The density of samples can be measured by the Archimedes principle. In order to characterize the thermal diffusion coefficient and specific heat capacity of the epoxy composites, the samples were analyzed by laser flash method (LFA447, NETZSCH, Germany). The experimental measurement set-up and the principle of laser flash method are illustrated in our previous study [16]. The thermal diffusion coefficient of samples can be obtained from output signal curves in LFA447. The output signal intensity is affected by the voltage of laser emission system and the pulse width of laser. The excessive voltage and pulse width of laser will cause the signal overflowing. In this test, the voltage of laser emission system was set at 270 V. The pulse width of laser light was set as “medium”. The testing temperature was set as 25 °C. Each sample was tested 5 times. In order to match the instrument, samples were required to shape their size to a diameter in 12.7 mm, and thickness in 2 mm of disks. Pyroceram9606 was chosen as the standard sample for getting results of specific heat capacity. All samples were ground flat on both sides and coated with a thin graphite layer to increase the absorption of the light flashes.

3. Results and discussions

3.1. Characterization of functional groups of modified ZrB_2/Al_2O_3

Fig. 3 shows the Fourier Transform Infrared (FT-IR) spectra of non-modified and γ-glycidoxypropyltrimethoxysilane functionalized ZrB_2/Al_2O_3 composite particles.

From the spectra analysis, it is clear that there are significant differences between two patterns. As shown in Fig. 3(a), non-modified composite particles exhibit clearly absorption bands below 710 cm^{-1}, which are considered to be related to Al—O and Al—O—Al bonding of Al_2O_3 [26] in ZrB_2/Al_2O_3. Besides, a broad and weak peak is observed at around 3440 cm^{-1} which is attributed to the presence of absorbed water and surface hydroxyl groups (—OH) on the surface of the alumina in ZrB_2/Al_2O_3 composite particles [27]. In comparison with Fig. 3(a), after the surface functionalization of ZrB_2/Al_2O_3 composite particles by the γ-glycidoxypropyltrimethoxysilane, see Fig. 3(b), the O—H stretching peak at 3440 cm^{-1} clearly sharpened and the intensity increased, meanwhile, a new sharp O—H bending peak at 1380 $cm^{-1}$is also observed, which demonstrates that the amounts of —OH group on the surface of functionalized particles increase. The possible reasons for the increase of —OH groups on the surface of modified particles are considered that the remaining —OH groups are resulted from the hydrolyzed γ-glycidoxypropyltrimethoxysilane attached on the surface of composite particles which are not covalently bonded onto the modified particles. The two new absorption peaks at about 1630 $cm^{-1}$and 1093 $cm^{-1}$are respectively attributed to the stretching vibration of Si—OH groups and bending vibration of Si—O—Si—R groups [28], which indicates that the γ-glycidoxypropyltrimethoxysilane had hydrolyzed and coupled onto the surface of composite particles. Also new weak absorption peaks at around 2917 $cm^{-1}$and 2840 cm^{-1} ascribed to asymmetrical and symmetrical stretching vibration of the C—H bond in methylene group produced from the silane are observed, further indicating that the silane exists on the surfaces of composite particles. After the surface functionalization of composite particles by γ-glycidoxypropyltrimethoxysilane, the characteristic absorption peaks of Al—O bond at about 720 cm^{-1} are broadened and blue shifted by a few wavenumbers (relative to the unmodified, as shown in Fig. 3(b)). The main reasons for the broadening and blue shift of Al—O can be regarded as a result of introduction of Si(R)OH into Al—O forming Al—O—Si(R)OH resulted from the chemical reaction of γ-glycidoxypropyltrimethoxysilane with composite particles and thus increasing the frequence of vibration of Al—O (blue shift) due to Si (electronegativity, 1.8) having stronger affinity to the elections than that of Al (electronegativity, 1.5). The chemical reaction mechanism includes the hydrolysis of γ-glycidoxypropyltrimethoxysilane forming reactive silanols (Si—OH) and then the condensation reaction between silanols groups producing the silanol oligomer. After that, the hydrogen bonds were first formed between the silanol oligomer and Al—OH groups from the surfaces of composite particles and then the Si—O—Al covalent bonds were formed by dehydration reaction after the drying. This can also be further confirmed by the emergence of characteristic absorption peaks of Al—O—Si at about 590 cm^{-1} [29] in Fig. 3(b). The chemical reaction mechanism can be illustrated schematically in Fig. 4.

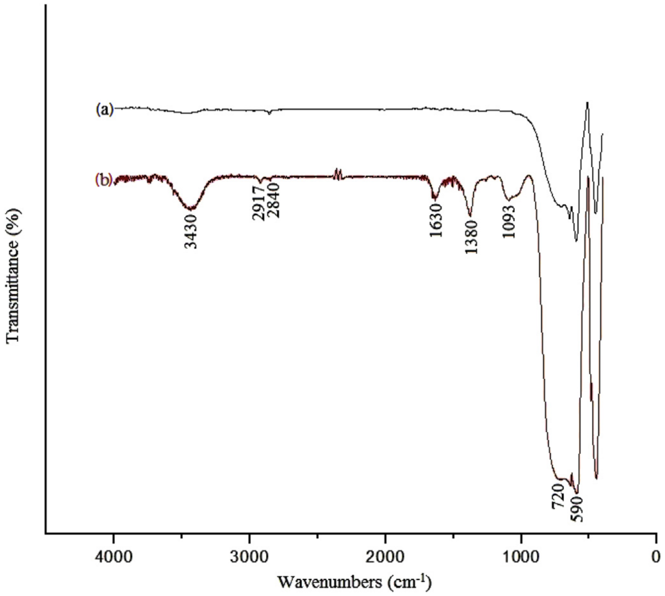

Fig. 3. FT-IR spectra of (a) unmodified ZrB_2/Al_2O_3 composite particles and (b) modified ZrB_2/Al_2O_3 composite particles.

In addition, the O—Si—O characteristic absorbing peak of γ-glycidoxypropyltrimethoxysilane appears also at around 1630 cm^{-1} [30], which makes the peak at 1630 cm^{-1}stronger. These results mentioned above indicate that ZrB_2/Al_2O_3 composite particles were successfully functionalized with functional groups of γ-glycidoxypropyltrimethoxysilane introduced on the surface of composite particles by the chemical reaction of the silane compound with composite particles and the chemical bonding of organosilane onto composite particles surfaces was realized through Al—O—Si bonds.

The X-ray photoelectron spectroscopy (XPS) was also used to characterize silane-functionalized ZrB_2/Al_2O_3 composite particles. Fig. 5(a) and (b) show the XPS spectra of non-modified and γ-glycidoxypropyltrimethoxysilane functionalized composite particles, respectively.

As shown in Fig. 5, after the surface functionalization of composite particles by the coupling agent (Fig. 5(b)), the binding energy of O1s,Si2p^3,Al2p and Zr3d^5 on the surfaces of composite particles is all decreased in different degrees compared to that of the non-modified composite particles. Before modification, their binding energy is respectively 534.00eV(O1s), 103.00 eV(Si2p^3), 76.00 eV(Al2p) and 184.00 eV(Zr3d^5), while, they are decreased to 531.00 eV, 101.00 eV, 74.00 eV and 181.00 eV after modification, respectively. Indicating that the chemical environment of element atoms on the surfaces of composite particles was changed and the peaks were also chemical shifted to the right (decrease) after the surface functionalization of composite particles. The analyses suggest that the change was mainly resulted from the functional groups from the silane introduced onto the surfaces of composite particles by the chemical reaction between the silane coupling agent and ZrB_2/Al_2O_3 composite particles. According to the above analysis of modified mechanism, after the surface functionalization of composite particles with γ-glycidoxypropyltrimethoxysilane, the hydroxyl groups on the surfaces of composite particles are substituted by the silane coupling agent molecules through the oxygen-bridge bonds, leading to the outer electron density of element atoms on the surfaces of particles increases and shielding effect enhances due to more stronger electrophobic effect possessed by the organic chains substitute portion than that of —OH group. As a result, the binding energy of inner electrons decreased, and thus the peaks were chemical shifted to the right.

Fig. 6 shows the SEM and energy dispersive spectroscopy (EDS)

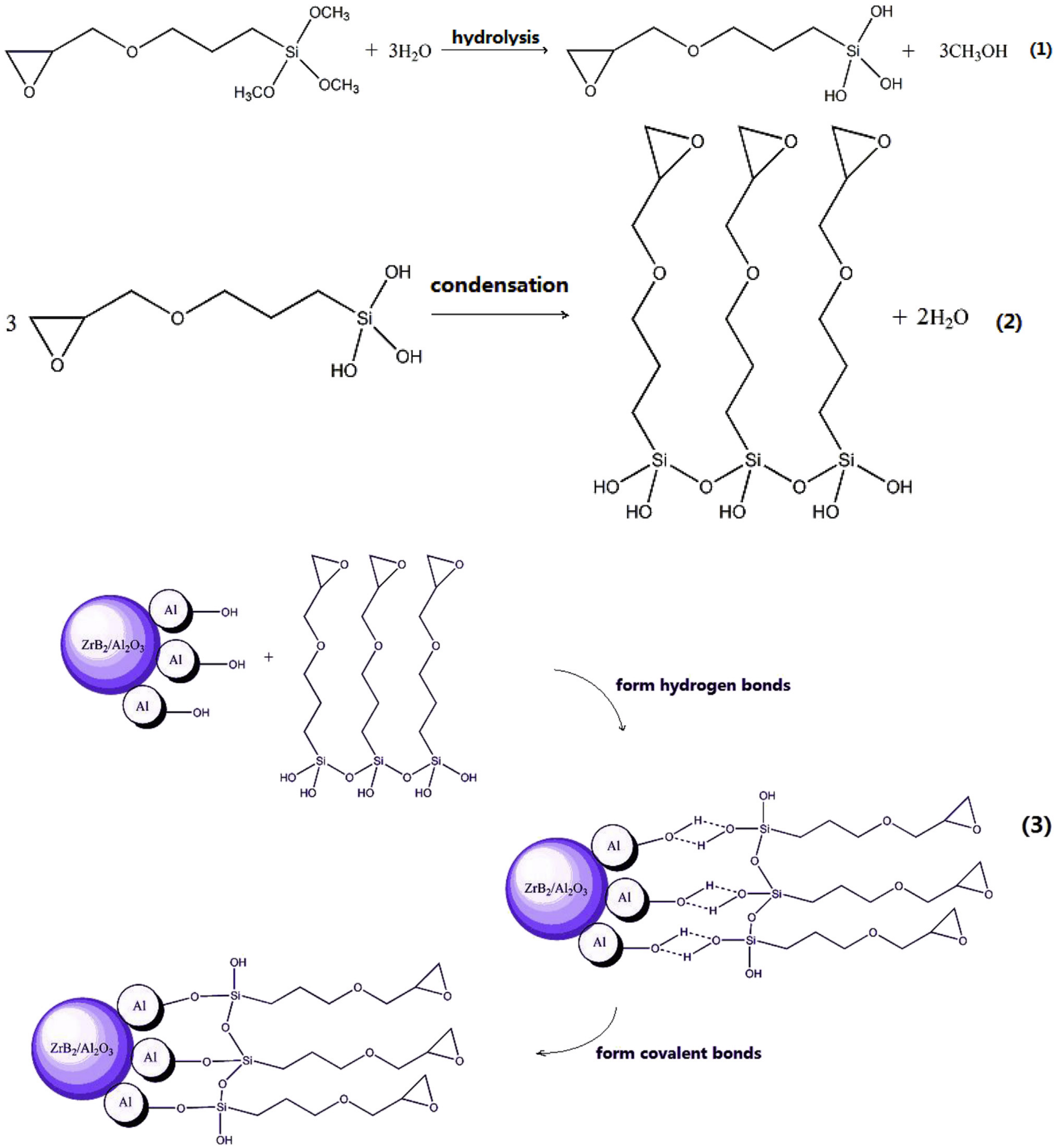

Fig. 4. The action mechanism of γ-glycidoxypropyltrimethoxysilane on ZrB_2/Al_2O_3 composite particles surface (1) hydrolysis of γ-glycidoxypropyltrimethoxysilane (2) condensation reaction between silanols groups (3) Formation of hydrogen bonds and covalent bonds.

of composite particles. As shown in Fig. 6(a) and (b), the composite powders are composed of two particles with different particle size. In order to define the chemical compositions, the EDS analysis of composite particles was conducted. Fig. 6(c) and (d) shows the EDS pattern of the particle A (larger) and B (smaller) in Fig. 6(a), respectively. As seen from them, particle A is a substance with a high zirconium and boron content, while particle B has a high aluminum and oxide content. According to the XRD analysis above, it can be defined that particle A is ZrB_2 and B is Al_2O_3. The non-modified composite particles present the agglomeration in some degree, and the particles have the portion of overlap more or less (Fig. 6(a)), while after functionalization, the modified particles are dispersed well and its individual particle can be distinguished (Fig. 6(b)). It is mainly resulted from γ-glycidoxypropyltrimethoxysilane on the surfaces of modified particles preventing agglomeration between two adjacent particles due to the decrease of surface energy of modified particles by the chemical reaction between SiOH groups from γ-glycidoxypropyltrimethoxysilane and the hydroxyls on the surfaces of the alumina nanoparticles of ZrB_2/Al_2O_3 composite particles, which results in a decrease of clustering

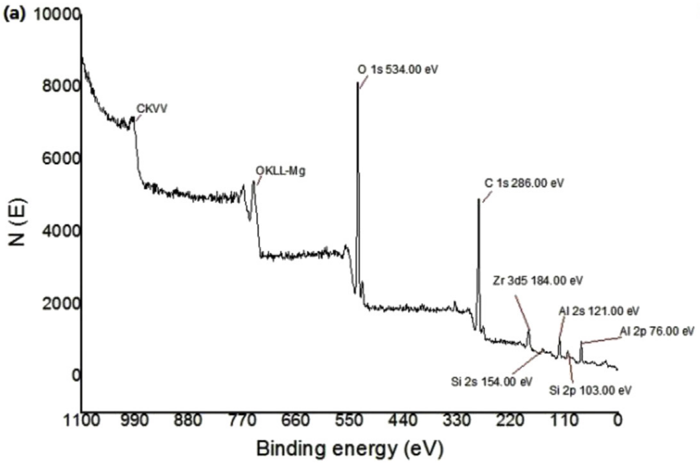

Fig. 5. X-ray photoelectron spectroscopy of (a) Non-modified ZrB_2/Al_2O_3 composite particles and (b) γ-glycidoxypropyltrimethoxysilane modified ZrB_2/Al_2O_3 composite particles.

tendency of particles.

3.2. Dispersion of ZrB_2/Al_2O_3 composite particles in epoxy matrix

It is critical to get good dispersion of fillers in composites for obtaining optimized performances. Fig. 7 shows TEM micrographs of the dispersion of 5 vol % ZrB_2/Al_2O_3 composite particles before and after functionalization in epoxy matrix. The comparison of Fig. 7(a) and (b) shows that the non-modified fillers mainly exist in the form of agglomerations in resin matrix, while the agglomerate size of modified fillers is reduced greatly, and a significant improvement in the particles distribution can be observed, which is mainly attributed to the surface treatment of the alumina parts in ZrB_2/Al_2O_3 by γ-glycidoxypropyltrimethoxysilane. It can be believed that ZrB_2/Al_2O_3 composite fillers are prone to agglomerate due to having higher specific surface area and surface energy, which makes it difficult to disperse in epoxy resin. After the functionalization, the surfaces of modified composite particles are covered by γ-glycidoxypropyltrimethoxysilane. On one hand, the surface energy of the particles is decreased by γ-

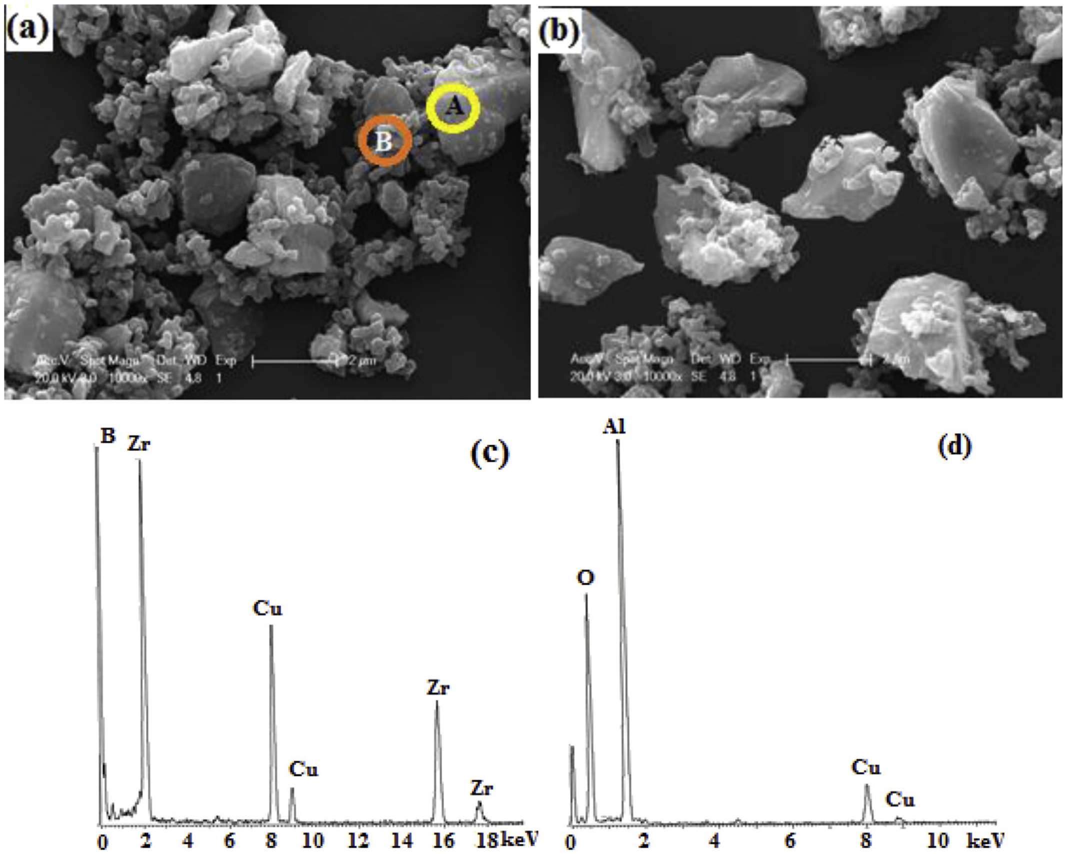

Fig. 6. SEM micrographs of (a) non-modified ZrB_2/Al_2O_3 composite particles, (b) γ-glycidoxypropyltrimethoxysilane modified ZrB_2/Al_2O_3 composite particles and EDS patterns of (c) the particle A and (d) B in Fig. 6(a).

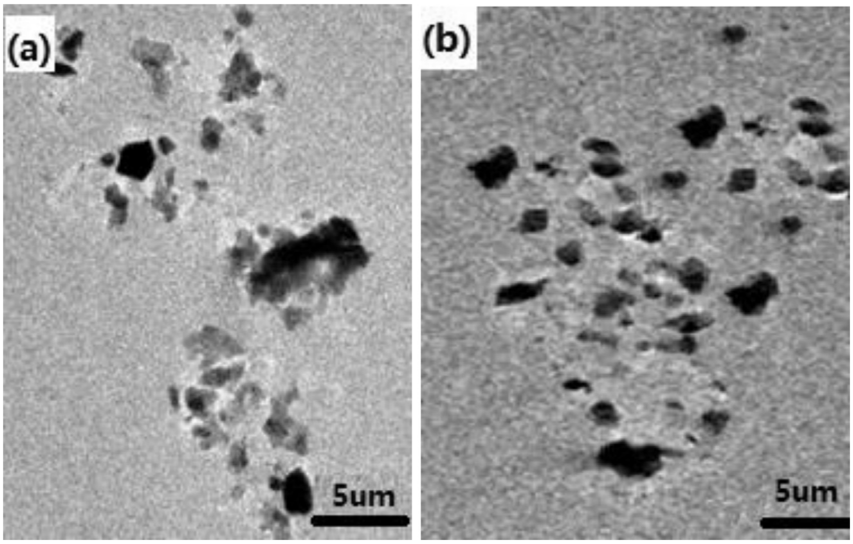

Fig. 7. TEM micrographs of (a) epoxy composite filled with 5 vol % non-modified ZrB_2/Al_2O_3 composite particles (b) epoxy composite filled with 5 vol % γ-glycidoxypropyltrimethoxysilane modified ZrB_2/Al_2O_3 composite particles.

glycidoxypropyltrimethoxy- silane through the chemical reaction between active groups of silane and composite particles, which results in a decrease of agglomeration of ZrB_2/Al_2O_3 composite fillers. On the other hand, more importantly, the surface group structure of the modified particles is more compatible with the epoxy resin than that of the original particles due to having the same epoxy groups in γ-glycidoxypropyltrimethoxysilane structure as in the epoxy resin, the modified particles disperse more easily and are more stable in epoxy resin.

3.3. Thermal conductivity of epoxy composites

The experimental results of thermal conductivities of epoxy composites were obtained by a laser flash method, as shown in Fig. 8.

In general, the thermal conductivity performance of polymer matrix composites is determined by heat-conducting properties of the filler itself and distribution state of the fillers in the matrix. As shown, the thermal conductivities of epoxy composites are obviously improved by the addition of ZrB_2/Al_2O_3 composite fillers because the thermal conductivities of ZrB_2 and Al_2O_3 components are much greater than that of neat epoxy. The thermal conductivities of epoxy composites filled with 5 vol% unmodified and modified fillers are 0.48 W/m·K and 0.54 W/m·K, increased by 212% and 251% relative to the neat resin, respectively. At low filler contents, the fillers are hardly in contact with each other and effective heat-conductive paths are scarcely created, thus the thermal conductivity of epoxy composites increases gradually with the increase of filler contents. The effective thermal conductivity of epoxy composites increases rapidly when the ZrB_2/Al_2O_3 composite fillers contents exceed 1 vol%. This could be explained that as the volume fraction of ZrB_2/Al_2O_3 composite fillers increase, the effective distribution of ZrB_2/Al_2O_3 composite fillers in the composites is enhanced, and good distribution of the particles develops more easily the conduction carrier path, resulting in a rapid increase of thermal conductivity.

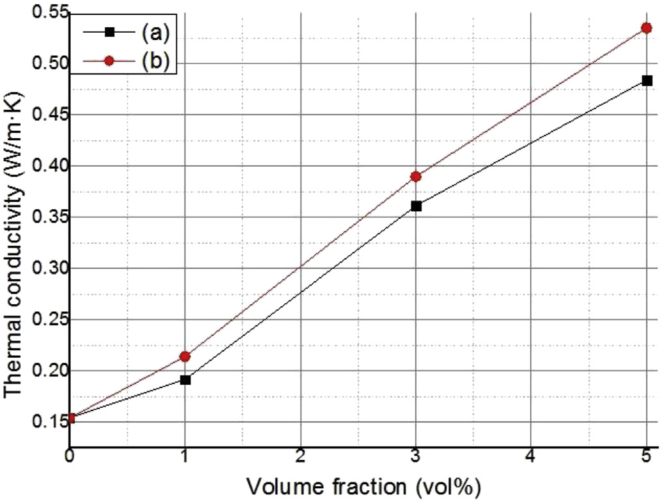

Fig. 8. The experimental results of thermal conductivities of epoxy composites filled with (a) unmodified and (b) modified ZrB_2/Al_2O_3 composite fillers.

In comparison, the effective thermal conductive performance of epoxy composites was improved in some degree due to the addition of γ-glycidoxypropyltrimethoxysilane modified particles. The thermal conductivities of functionalized composites with 3 vol% and 5 vol% loading are 0.39 W/m·K and 0.54 W/m·K, increased by 8.3% and 12.5% relative to the unmodified composites, respectively. As analyzed above, the organic functionalization improves the interfacial compatibility and dispersion of composite particles in epoxy matrix, and enhances the interfacial bonding. It leads to the reduction of interface resistance and helps to diffuse heat more effectively.

3.4. Application of thermal conductive model to experimental data

Using the finite-element program ANSYS, thermal analysis is carried out for the heat conductive transfer through the epoxy composites. In order to operate the thermal analysis, three-dimensional models have been used to simulate the microstructure of composite materials for various filler contents ranging from 1 vol% to 5 vol%. In finite element models, the effective thermal conductivities of composites were calculated by Fourier's law of heat conduction. According to the conditions in this study: 3-D space (x, y, z), heat field, no mass transportation, in steady status the equation to calculate thermal conductivity can be expressed as:

$$-Q = \frac{\partial}{\partial x}\left(K_{eff}\frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_{eff}\frac{\partial T}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_{eff}\frac{\partial T}{\partial z}\right) \tag{2}$$

Where T is the temperature in K, K_{eff} is the effective thermal conductivity in $W \cdot m^{-1} \cdot K^{-1}$ and Q is the heat generation rate per unit area in $W \cdot m^{-2}$. Thus, the effective thermal conductivities can be obtained from the values of thermal flux and the thermal gradient of composites in ANSYS.

In the finite element analysis of the heat conduction, the composites are consisted of epoxy matrix and ZrB_2/Al_2O_3 composite fillers. The epoxy matrix are assumed as cubic and ceramic fillers are assumed as spherical. In finite element models, the particle sizes are dimensionless. The size ratio of ZrB_2 and Al_2O_3 particle is the key factor which influences the simulated results in FEMs. Since the main effect of Al_2O_3 in this work is used for the firm connection between ZrB_2 and epoxy resin, the diameter of ZrB_2 particle is set as ten times of that of Al_2O_3 particle. The Al_2O_3 particles are dispersed randomly on the surfaces of ZrB_2 particles and the distribution of the binary fillers is random in the epoxy matrix. All ingredients are assumed to be isotropic and homogeneous with temperature independent. To understand the improvement of the thermal conductivity of the epoxy resin by the fillers directly, the thermal conductivity of neat epoxy resin was measured as 0.154 W/m·K at room temperature and it is a little lower than that of the previous report [31], which could be due to the system errors of the thermal conductivity analyzer or the sample with some defects from the preparation process. The values of thermal conductivities of ZrB_2 and Al_2O_3 at room temperature are about 57.9 W/m·K and 30.0 W/m·K, respectively [32,33]. The two interfaces of ZrB_2–Al_2O_3 and Al_2O_3-epoxy are considered with isotropic and temperature independent properties. The thermal conductivities of the interfaces are assumed to be the average of those of neighboring ingredients [34]. To be specific, the thermal conductivities of ZrB_2–Al_2O_3 and Al_2O_3-epoxy interface are assumed as 43.95 W/m·K and 15.077 W/m·K, respectively. The representative volume element (RVE) consists of a part of the epoxy composites, including cubic epoxy resin matrix, spherical ceramic fillers, and appropriate interfaces. All Al_2O_3 particles are assumed to connect ZrB_2 particles well.

The boundary conditions to apply vertical loading on the RVE include one surface loaded by heat and the other five surfaces occurring convection with isothermal atmosphere. The temperatures of heat loading and atmosphere are set as 100 °C and 20 °C, respectively. The finite element type of the RVE of both matrix and fillers is the SOLID278 which has eight nodes in prism option with one degree of freedom, temperature, at each node in the commercial software ANSYS. The number of the elements which stands for the level of discretization is set as over three million in each model.

The thermal conductive performance of epoxy composites is affected by the distribution of the fillers obviously. In order to reduce the calculated errors caused by the contingency of the distribution of fillers, the simulated effective thermal conductivities of all epoxy composites filled with ceramic fillers are calculated 10 times at each volume fraction, and the calculated results of thermal conductivities of epoxy composites are presented in the mean values. Fig. 9 presents comparative curve graphs of the mean values of thermal conductivities and experimental results. As shown, the change tendency of calculated results of thermal conductivities of epoxy composites accords with that of the experimental results. The simulated results are in reasonable agreement with experimental results basically. Almost all the relative difference of the values of FEM and experimental measurements is under 5% (defined experimental values as the true values). There are slight errors between calculated and experimental thermal conductive values of epoxy composites. It is resulted from the ideal assumptions in the finite element models mentioned above.

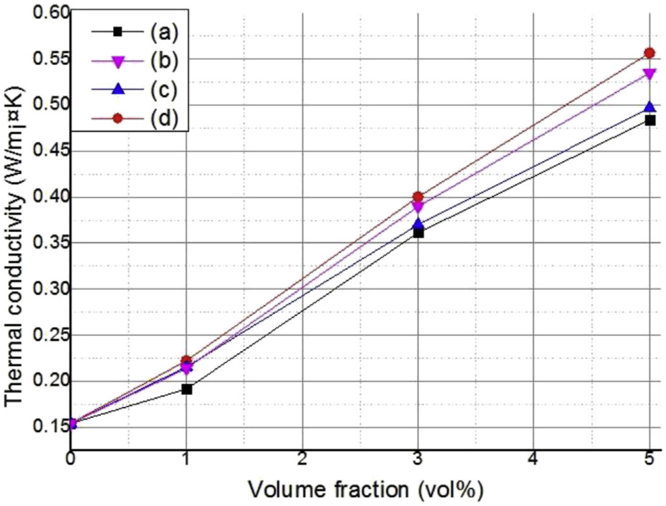

Fig. 9. Comparison of experimental values and FEA values of the thermal conductivities of epoxy composites filled with non-modified ZrB_2/Al_2O_3 composite fillers (a), (c) and modified ZrB_2/Al_2O_3 composite fillers (b), (d).

The effect of the Al_2O_3 particles attached to the ZrB_2 particles could be regarded as the stretch of ZrB_2 particles. This stretch is helpful to diffuse heat in the epoxy composites more effectively. However, the effects of the additions of the multiphase ceramic fillers on improvement of thermal conductive performances of epoxy composites are limited. At high volume fractions, the fillers in experimental samples have less space to disperse. The ceramic fillers could form the agglomerates in the epoxy matrix due to the poor compatibility between organic matrix and inorganic fillers. It reduces the heat diffusive effects of non-modified ZrB_2/Al_2O_3 composite fillers in epoxy composites. With the introduction of silane coupling agents, the compatibility between epoxy matrix and ceramic fillers and the dispersion of fillers are improved. According to Fig. 7(a) and (b), the introduction of γ-glycidoxypropyltrimethoxysilane can reduce the agglomeration of fillers, which results in the higher thermal conductivity of epoxy composites filled with modified ZrB_2/Al_2O_3 composite fillers than that of non-modified fillers.

In Fig. 10, the heat conduction status of the interfaces is shown with heat vector diagram in cross-section. The heat flux is mainly conducted by ceramic fillers in the epoxy composites.

According to the density of heat flux, the interfaces can diffuse heat effectively. The heat is loaded from bottom to top in the composites. The ZrB_2 filler, absorbing the heat from matrix, can transfer heat to the Al_2O_3 filler via the ceramic interface. The corners of ceramic interface can transfer more heat than the center part of the ceramic interface. It shows that the ceramic interface can absorb heat of the ZrB_2 filler around, and conduct heat effectively. On the other hand, the coupling agent can form a transition layer on the interface between Al_2O_3 and epoxy matrix. The heat can be diffused by the transition layer connecting organic and inorganic ingredients from Al_2O_3 to epoxy matrix, which contributes to the temperature homogenization of composites and the improvement of thermal conductive performance of whole epoxy composites. According to the comparison of the interface between ZrB_2 and epoxy matrix, and the coupling agent layer, the direction and density of heat vectors in the ZrB_2 prove that the heat exchange between ZrB_2 and epoxy is poor. Indicating that the introduction of transition layers on the interfaces between organic matrix and inorganic fillers is crucial to the improvement of the thermal

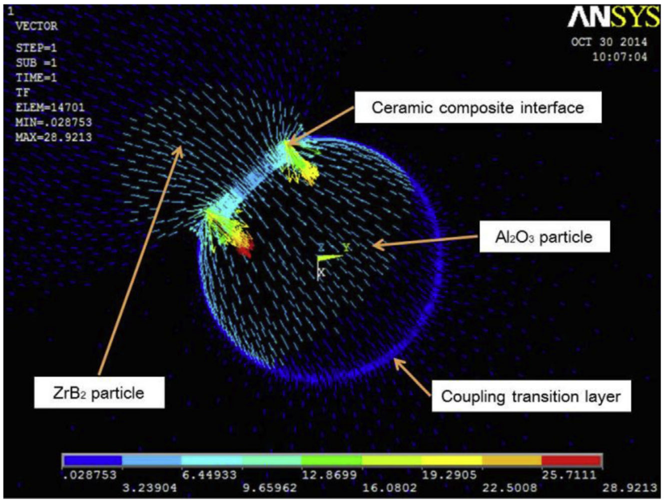

Fig. 10. The schematic of heat vectors of epoxy composites filled with γ-glycidoxypropyltrime- thoxysilane modified ZrB_2/Al_2O_3 composite fillers.

conductive performance of epoxy composites.

The interface resistance blocks the heat conduction in composite systems. In the epoxy composites filled by ZrB_2/Al_2O_3 composite fillers, ceramic composite forms coherent or semi-coherent interface [17], which can reduce interface resistance and transfer heat effectively between ZrB_2 and Al_2O_3 particles. With the introduction of γ-glycidoxypropyltrimethoxysilane, chemical bonds are formed between modified Al_2O_3 particles and epoxy resin [35]. The chemical bonds can enhance the interfacial bonding and reduce the interface resistance between epoxy matrix and ceramic fillers. It helps to improve thermal conductive performance of epoxy composites further.

4. Conclusions

Boride ceramics are very promising to increase the thermal conductivity of polymer composites because of their great heat-conducting properties. The surface covalent functionalization for improving dispersion and interfacial bonding is an effective means to take full advantage of the exceptional thermal performances of ZrB_2 ceramics. The study results indicate that ZrB_2/Al_2O_3 composite ceramic particles organic functionalization could be achieved by silanization process through Al—O—Si chemical bond. Functionalized ZrB_2/Al_2O_3 composite particles present better dispersion and interfacial bonding in the composites. The thermal conductive performance of epoxy composites is improved by filling with ZrB_2/Al_2O_3 composite fillers. In comparison, after surface functionalization of ZrB_2/Al_2O_3, functionalized composites reveal more better thermal conductivities due to more effective diffusion heat of the modified fillers in even dispersion. 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. Showing that the thermal resistance of interfaces is reduced due to the surface functionalization, and then, the heat could be dissipated more effectively through the modified interfaces of ZrB_2/Al_2O_3 and epoxy matrix. Most of the relative difference of the values of FEM and experimental measurements is under 5%. The finite-element analysis results are in reasonable agreement with experimental data. The results could be very useful for investigation on the potential of high-performance boride ceramics for use in the tailor of advanced heat-conduction polymer matrix composite materials.

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