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ORIGINAL PAPER

Preparation and mechanical properties researches of silane coupling reagent modified β-silicon carbide filled epoxy composites

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Abstract The β-silicon carbide (β-SiC) micro particles modified by silane coupling reagent of γ-glycidoxy propyl trimethoxy silane (KH-560) were employed to prepare β-silicon carbide/epoxy resin (SiC/EP) by blending-casting moulding method to acquire polymer composites with high mechanical properties. Mechanical tests demonstrate that, both the flexural and impact strength of the composites increased firstly with the increasing content of SiC, but decreased with excessive addition of SiC. When the mass fraction of SiC was 10%, the mechanical properties of SiC/EP composites were maximum. Meantime, the use of SiC particles modified by KH-560 significantly enhanced mechanical properties of SiC/EP composites. The surface performance of SiC was characterized and analyzed by XPS, FTIR and TGA. The results indicated that a chemical bonding formed between KH-560 and SiC, and a layer of organic single molecule membrane formed on the surface of SiC. And the maximum mass fraction of KH-560 coated on the surface of SiC was about 2.62%.

Keywords Epoxy resin · Silicon carbide · Composites · Surface modification

Introduction

Epoxy resins have been established as a class of high performance thermosetting polymers widely applied as matrix of coatings, adhesives and composites [1–3], due to their high mechanical properties, excellent dimensional and thermal stabilities

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and environmental stability. SiC is composed of two types of crystal structures, i.e. α-SiC (hexagonal structure) and β-SiC (face-center-cubic structure), and the mechanical properties of the latter is better than that of the former. β-SiC possesses excellent properties, such as high strength and modulus, high temperature and corrosion resistance, and thermal shock and wear resistance, which has been widely used in the preparation of high-performance composites [4–7].

Surface modification is an effective method to improve the mechanical properties of SiC/EP composites. Silane coupling reagent of γ-glycidoxy propyl trimethoxy silane (KH-560) is an important coupling reagent, which can form a layer of single molecule membrane on the surface of fillers and improve the wettability and dispersion of them. SiC particles modified by KH-560 were employed to prepare SiC/EP composites by blending-casting moulding method in this research. Mechanical tests showed that, both flexural strength and impact strength of the composites increased firstly with the increasing content of SiC, but decreased with excessive addition of SiC. When the mass fraction of SiC was 10%, the mechanical properties of SiC/EP composites were maximum. The surface performance of SiC was characterized and analyzed by XPS, FTIR and TGA. The results indicated that a chemical bonding was formed between KH-560 and SiC, and a layer of organic single molecule membrane was formed on the surface of SiC. Moreover, the maximum mass fraction of KH-560 coated on the surface of SiC was about 2.62%.

Experimental

Materials

Epoxy resin (E-51), bisphenol-A (structural formula in Fig. 1), was supplied from Wuxi Resin Factory of Blue Star New Chemical Materials CO., Ltd (Jiangsu, China); β-SiC (face-center-cubic structure), with grain diameter of 1–2 μm, a density of 3.2 g/cm^3, specific surface area of 2.5 m^2/g (Fig. 2), was supplied from Xuzhou Hongwu Nanomaterial Co., Ltd. (Jiangsu, China); Hexahydrophthalic anhydride (HHPA), was supplied from Xi'an Hangang Chemical Group Co., Ltd. (Shaanxi, China); silane coupling reagent of γ-glycidoxy propyl trimethoxy silane (KH-560) was supplied by Nanjing Shuguang Chemical Group Co., Ltd. (Jiangsu, China); isopropyl alcohol and ethyl alcohol were supplied from Tianjin Ganglong Chemical Group Co., Ltd. (Tianjin, China).

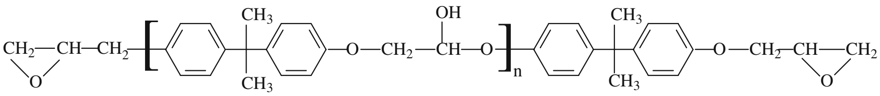


Fig. 1 Structural formula of EP-51

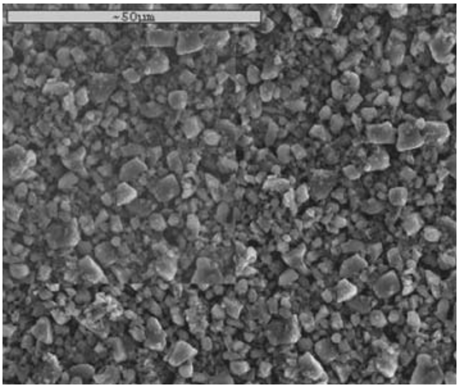
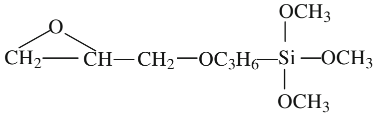


Fig. 2 SEM microscopy of *β*-SiC

Surface modification of SiC fillers

Silane coupling reagent of *γ*-glycidoxy propyl trimethoxy silane (KH-560) was introduced to ensure good dispersion and improvement of interface between SiC and epoxy resin. And the chemical structure of KH-560 is as below.



$$CH_2(O)CH-CH_2-OC_3H_6-Si(OCH_3)_3$$

The SiC surface modification was carried out as follows:

(1) the mixtures of SiC, KH-560, ethanol and water solvent with proper prescription were mixed in a reactor
(2) reacting for 4 h (80°C, pH 9) with stirring, and placed for 24 h at room temperature
(3) drying in vacuum for 18 h to remove solvent at 100°C. The modified SiC was kept at 80°C in order to protect the SiC surface from water.

Preparation of SiC/EP composites

The epoxy resin, HHPA and the SiC fillers were mixed in a mixing machine for more than 30 min firstly, the mixtures above were kept in a vacuum vessel to remove voids, and then poured into the preheated die. It was cured in a vacuum oven according to the procedure of: 100°C/1 h + 120°C/2 h + 150°C/4 h, followed by post-curing in vacuum oven at 190°C for 4 h.

Measurement and characterization

The X-ray photoelectron spectroscopy (XPS) analysis of samples was carried out by PHI5400 equipment (Perkin–Elmer, USA) to measure element components and the differences of electron binding energy of SiC.

Fourier transformed infrared spectroscopy (FTIR) (Nicolet-550, Nicolet Co. USA) was employed using thin KBr as the sample holder. Transition mode was used and the wavenumber range was set from 4,000 to 400 cm^{-1} (resolution 1 cm^{-1}, measuring time 300 s).

Thermal-gravimetric analyzer (TGA) measurement was performed on Q50 instrument (TA instruments, USA). About 10.0 mg sample was put in alumina crucible and heated from the heating rate was set as 10°C/min (nitrogen atmosphere, flow rate of 150 ml/min).

Flexural properties were measured by Electron Omnipotence Experiment Machine SANS-CMT5105 (Shenzhen New Sansi Corp., China) according to standard ISO178-1993. The impact strength of the samples was measured with ZBC-4B impact testing machine (Shenzhen New Sansi Corp., China) according to standard ISO179-1993.

Results and discussion

Mechanical properties of SiC/EP composites

The mass fraction of SiC influencing on mechanical properties of cured SiC/EP composites are presented in Fig. 3. The addition of SiC can enhance both impact strength and flexural strength of EP resins. When the mass fraction of SiC is increasing, both flexural and impact strength of the composites are also increased. When the mass fraction of SiC is 10%, the flexural strength is increased from 108.7 to 118.7 MPa, and the impact strength of composites is enhanced from 13.6 to 14.5 kJ/m^2.

The results are ascribed that SiC can remedy the defects from epoxy self-curing. In addition, the oriented structure of SiC can transfer stress and prevent the expanding of crazing, thus to increase cohesive strength, decrease weak process links and improve mechanical strength of composites. With the excessive addition of SiC, the viscosity of epoxy resin increases, the dispersion of SiC gets worse, gas bubble and excessive stress concentration points are easy to form, consequently,

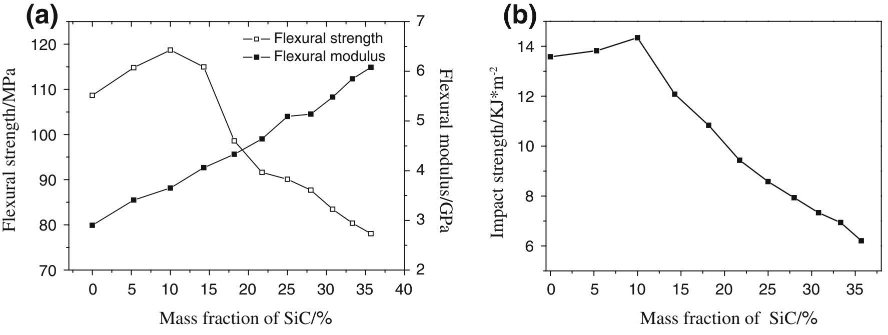


Fig. 3 The content of SiC influencing on mechanical properties of SiC/EP composites. **a** Flexural strength and flexural modulus. **b** Impact strength

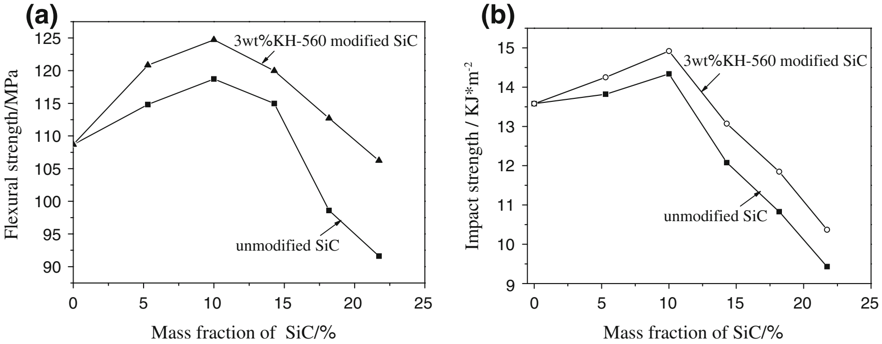


Fig. 4 The coupling reagent influencing on mechanical properties of SiC/EP composites. **a** Flexural strength. **b** Impact strength

result in the mechanical properties decline. However, the flexural modulus of composites increases gradually with the mass fraction of SiC, it can be attributed to the rigidity of SiC.

Figure 4 shows the coupling reagent influencing on the flexural strength and impact strength of SiC/EP composites. Both the flexural and impact strength of composites increase with at a fixed content of modified SiC. It is due to the good physical adsorption between modified SiC and epoxy resin that enhances the interface adhesion strength. Furthermore, alkoxy group in KH-560 can react with hydroxyl-terminated groups of epoxy resin, and improve the compatibility of SiC and epoxy resin, finally increase mechanical properties of the composites.

Effect of KH-560 on the interface of composites

X-ray photoelectron spectroscopy is employed to measure the surface element components and the differences of electron binding energy of samples [8–10]. According to the entire XPS scanning of modified SiC and native SiC, the content of various elements can be calculated by sensitivity factor, and the corresponding results are listed in Table 1.

It can be seen that, native SiC has been partially oxidized to form SiO_2. There is amount of oxygen element and some nitrogen impurity exists on the SiC surface. The Si2p peak and O1s peak recede significantly, and N1 s peak almost disappears, it can be attributed to the coverage of KH-560 on the surface of SiC.

Table 1 Concentrations of various elements on β-SiC surface

	Concentrations of various elements (%)			
Samples	C	O	Si	N
Native SiC	50.79	21.09	24.50	3.62
3 wt% KH-560 modified SiC	59.03	17.14	23.53	0.29

The C1s and Si2p peaks of modified SiC can be fitted using Gaussian–Lorentzian function, and the contents of C, Si and other possible groups are calculated according to the square of various peaks, shown in Tables 2 and 3.

The results show that the –C–Si– peak decreases at 283.44 eV, and it accounts for 22.13% of C, the corresponding peaks of –C–C– and –C–O– bonds of KH-560 account for 57.16% and 20.71% of C, respectively. Meantime, the modification of SiC makes Si2p peak lower. The devolution of the Si2p shows that the binding energy of 37.66% of Si increases by 2.59 eV. It can be deduced that the increasing binding energy of 37.66% of Si is ascribed to a chemical binding of –C–O–Si–.

Figure 5 shows FTIR spectra of native SiC, KH-560 and 3 wt% KH-560 modified SiC. It can be seen that, the FTIR spectrum of native SiC only presents a few absorption peaks. The bands at 500–680 cm^{-1} and near 1,100 cm^{-1} can be assigned to the characteristic vibration peaks of Si–C and Si–O groups, respectively.

Table 2 Components of C1s spectra of modified SiC

Number of C1s sub-peaks	Peak position (ev)	FWHM	XAT (%)	Corresponding group
C1	283.44	1.60	22.13	–C–Si–
C2	284.60	1.53	57.16	–C–C–
C3	285.74	1.60	20.71	–C–O–

Table 3 Components of Si2p spectra of modified SiC

Number of Si2p sub-peaks	Peak position (ev)	FWHM	XAT (%)	Corresponding group
Si1	100.73	2.09	62.34	–C–Si–
Si2	103.32	1.90	37.66	–C–O–Si–

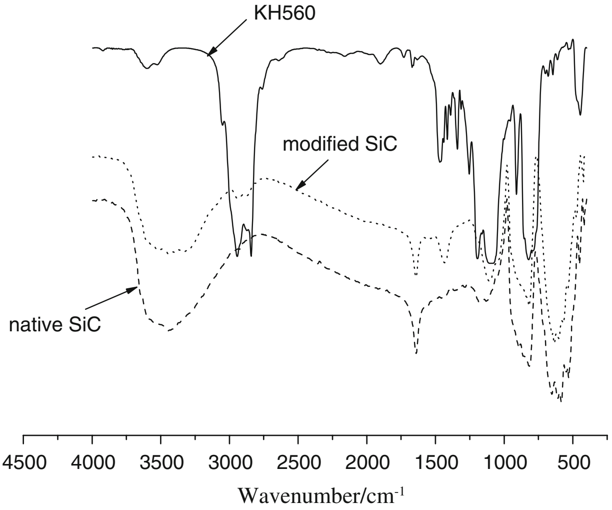


Fig. 5 FTIR spectra of native SiC, KH-560 and modified SiC

The characteristic stretching vibration peak at 3,447 cm^{-1} (–OH) can be attributed to water-absorption on the surface of SiC. The characteristic stretching vibration peak of C–H at 1,380 cm^{-1} appears after modification of SiC, and the characteristic stretching vibration peaks of organic methylene C–H bands at 2,917 and 2,851 cm^{-1} appear. In addition, characteristic absorption peak at 1,050–1,090 cm^{-1} broadens, the phenomenon reveals that a new absorption peak of Si–O–Si has formed at the range of 1,050–1,090 cm^{-1}, which is due to the contribution of interaction between siloxane and SiC. The interpretations above are enough to manifest that KH-560 is bound on the surface of SiC.

Figure 6 shows the TGA curves of native SiC and 3 wt% KH-560 modified SiC. It can be seen that, the weight loss of native SiC is 0.62% at the range of 0–400°C, and has almost no weight loss over 400°C. It is mainly due to the loss of absorbed water or hydroxy on the surface of SiC. The weight of modified SiC decreases quickly over 290°C, which can be attributed to the loss of water, the oxidation or thermal cracking of KH-560 at high temperature, and the weight loss of modified SiC is 3.24% over 500°C. By comparison with TGA curves, it can be deduced that the maximum mass fraction of KH-560 on the surface of SiC is about 2.62%.

Coupling mechanism analysis

Best of our knowledge, the coupling mechanisms mainly include chemical bonding and hydrogen theory and physical absorption model [11]. Based on the model of Arkles and the analysis above by XPS, FTIR and TGA, we can deduce the corresponding possible reactions among SiC, KH-560 and epoxy resin, as shown in Figs. 7, 8 and 9.

It can be concluded that KH-560 reacts with free proton on the SiC surface and forms firm chemical bond at one end. Its alkoxy group reacts with epoxy and hydroxyl-terminated groups of epoxy resin at the other end. Thus, the organic interface layer between SiC and epoxy resin is generated.

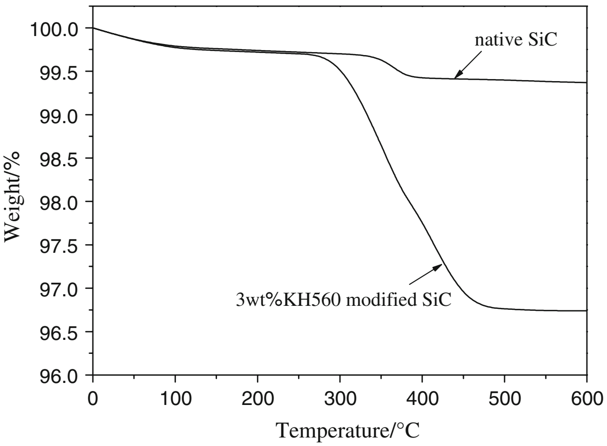


Fig. 6 The TGA curves of native SiC and modified SiC

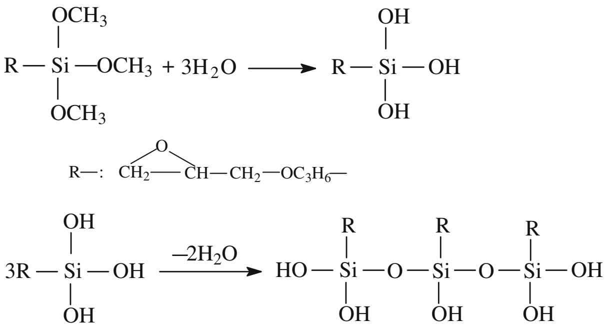


Fig. 7 The hydrolyzation and condensation of KH-560

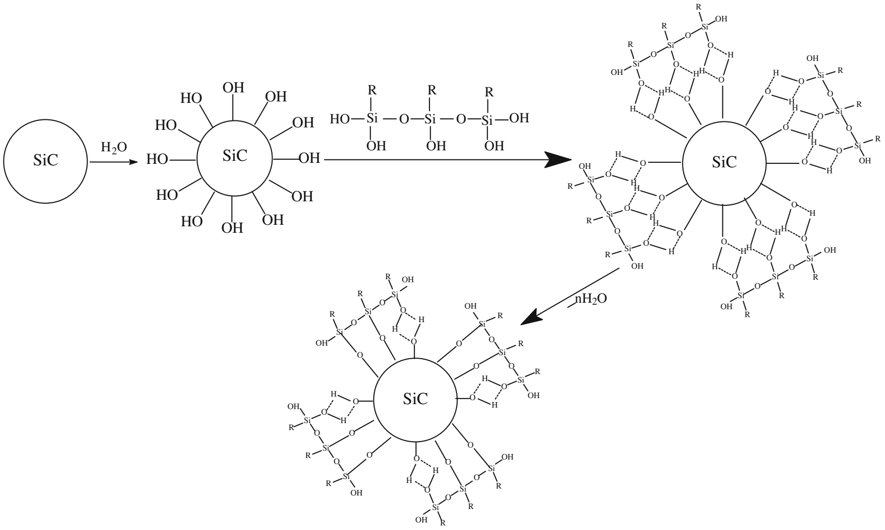


Fig. 8 Comprehensive Arkles model of chemical bonding-hydrogen-physical absorption between SiC and KH-560

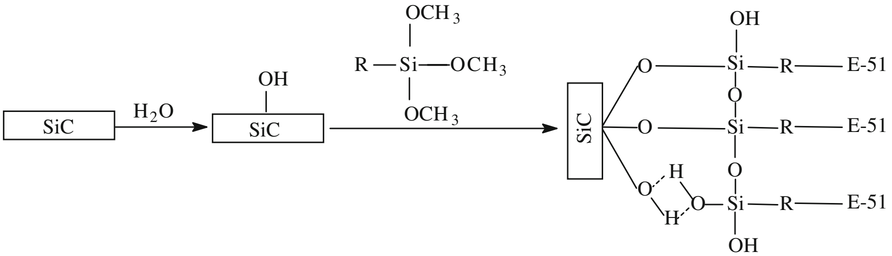


Fig. 9 Possible reaction among KH-560, SiC and epoxy resin

Conclusions

Mechanical tests showed that, both flexural strength and impact strength of the SiC/EP composites increased firstly, but decreased with excessive addition of SiC. When mass fraction of SiC was 10%, the mechanical properties of SiC/EP composites were maximum. Meantime, the use of SiC particles modified by KH-560 significantly enhanced mechanical properties of SiC/EP composites. XPS, FTIR and TGA analysis indicated that a chemical bonding formed between KH-560 and SiC fillers, and a layer of organic single molecule membrane formed on the surface of SiC. The maximum mass fraction of KH-560 on the surface of SiC measured is about 2.62%.

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