

# Synthesis and Characterization of Epoxy Resin Modified with $\gamma$ -Thiopropyl Triethoxy Silane

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**ABSTRACT:** Organic/inorganic hybrids with 1 to 7% silica contents were synthesized from bisphenol-A and epichlorohydrin by utilizing  $\gamma$ -thiopropyl triethoxy silane (KH580). The reactive coupling agent KH580 was introduced to epoxy resin to obtain high adhesive strength material for engineering industry. It was hypothesized that the multiple reactive functional silanol group Si—OH of KH580 after hydrolyzing reacted with epoxy resin to increase the shear strength and toughness of epoxy resin. IR spectra indicated that bonded stationary phase was

formed. Shear strength of epoxy resin-based composite increased and then decreased after SiO<sub>2</sub> content reached 5 wt %; the optimal value was 24.78 MPa. SEM analysis showed that toughness of SiO<sub>2</sub>/epoxy resin-based composite also increased and then decreased when the content of SiO<sub>2</sub> is more than 5 wt %. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2388–2394, 2009

**Key words:** epoxy resin;  $\gamma$ -thiopropyl triethoxy silane; adhesive strength; toughness

## INTRODUCTION

Organic–inorganic polymer hybrid materials have received a great deal of attention in recent years.<sup>1,2</sup> The hybrids are composed of organic and inorganic elements, and the intimate mixing provides various properties such as hardness, abrasion, adhesive strength, etc., resulting in the wide use in coatings, rubbers, plastics, sealants, fibers, etc.<sup>3,4</sup> Synthesis and characterization of organic–inorganic hybrid materials have received more and more considerable attention. Organic–inorganic hybrid materials can combine remarkable properties of inorganic phase and organic polymer. They require adhesives with high intensity and toughness, good anticreep performance, good fatigue resistance, and good shear resistance.<sup>5–8</sup>

Epoxy (EP) adhesives have been extensively used to fasten bridges and buildings in civil engineering because they are high in adhesive strength, low in shrinkage, high in corrosion resistance, and simple in processing. However, it is well known that epoxy resins are brittle after being cured, so it is necessary to toughen epoxy adhesives.

Many efforts have been made to improve properties of epoxy resin. In recent years, intensive research efforts have been devoted to the develop-

ment of epoxy resin. Lu et al.<sup>9</sup> prepared epoxy/titania/silica ternary hybrid materials with covalent bonding interaction between polymer and inorganic phases using titania/silica mesoporous particles, which were prepared by the sol–gel process from tetraethoxysilane (TEOS) and titanium tetra-butyltitanate (TBT) as precursors. The experiment results showed that the modulus of the modified systems decreases by adding mesoporous SiO<sub>2</sub>-TiO<sub>2</sub> particles to the epoxy matrix; the impact strength and tensile strength of the hybrid materials increase by 53.5 and 14% when the SiO<sub>2</sub>-TiO<sub>2</sub> content is up to 3 wt %. However, in this study the synthesis method is too complicated, which contains two steps. The first step is the preparation of polymer hybrids containing mesoporous titania and silica particles, which start from hybrid xerogels containing polyethylene glycol as a pore-forming agent. The second step is preparation of EP, and then mixing those together.

Chang et al.<sup>10</sup> prepared a series of hybrid materials consisting of epoxy resin matrix and well-dispersed amino-modified silica (AMS) nanoparticles. AMS nanoparticles were synthesized by performing the conventional acid-catalyzed sol–gel reactions of tetraethyl orthosilicate (TEOS), which acts as acceded sol–gel precursor in the presence of 3-aminopropyl trimethoxysilane (APTES), a silane coupling agent molecules. Good dispersion capability of AMS nanoparticles in hybrid materials was found to lead to enhanced mechanical properties. However, the process is also complicated.

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Therefore, in this study, we made an attempt to investigate the preparation of polymer hybrids containing SiO<sub>2</sub> particles by directly introducing KH580 into the process of synthesizing EP without any surface treatment, which predigests the traditional method needing two steps to modify epoxy resin. The obtained SiO<sub>2</sub>/EP hybrid materials were investigated by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM). The effects of silica contents on the properties of SiO<sub>2</sub>/EP hybrid materials such as mechanical properties were investigated.

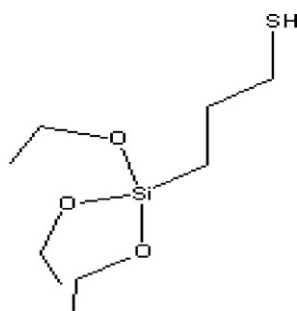
## EXPERIMENTAL

### Materials

Bisphenol A (chemically pure grade) was supplied by the Guoyao Chemical Reagent (Tianjin, China). 3-Chloro-1,2-epoxypropene (chemically pure grade) was purchased from Kemiou Chemical Reagent (Tianjin, China). NaOH (chemically pure grade) was purchased from Shanghai Chemical Reagent (Shanghai, China). Benzyltrimethylammoniumchloride (C<sub>10</sub>H<sub>16</sub>NCl) was supplied by Chendu Kelong Chemical Reagent (Chendu, China). Coupling agent (KH-560) was supplied by Hunan XiangTan Coupling Agent (Hunan, China).  $\gamma$ -Thiopropyl triethoxy silane (KH580) was provided by the Chemical Factory of Wuhan University (Wuhan, China).

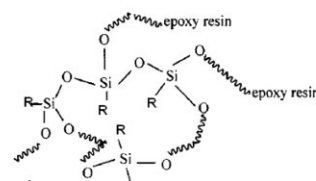
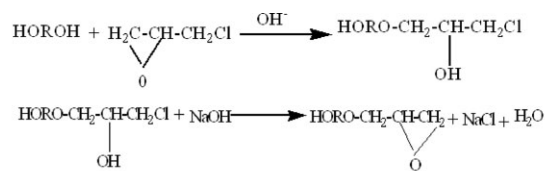
### Preparation of epoxy/SiO<sub>2</sub> composites

A practical problem in the preparation of composites is to disperse inorganic particles into organic medium on a homogenous scale. Some workers have reported the usefulness of coupling agents to prepare epoxy hybrid materials.<sup>11,12</sup> Coupling agents with various functional groups such as amido, epoxy, vinyl, and allyl groups can be incorporated into the hybrids to provide chemical bonding between organic and inorganic phases, thereby preventing phase separa-

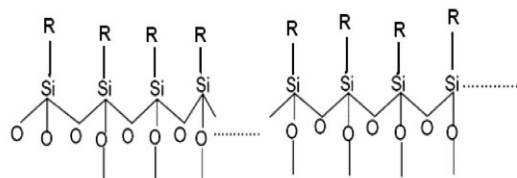


**C<sub>9</sub>H<sub>22</sub>O<sub>3</sub>SSi(KH580)**

**Scheme 1** Chemical structures of compounds.



**Reaction between KH580 and epoxy resin**



**Stationary bonding phase between C<sub>9</sub>H<sub>22</sub>O<sub>3</sub>SSi(KH580) and epoxy resin**

**Scheme 2** Synthetic steps of epoxy resin-based composites: R:—CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH.

tion and conglomeration of inorganic particles and obtaining homogenous composites.

In this research, C<sub>9</sub>H<sub>22</sub>O<sub>3</sub>SSi (KH580) containing three-silanol group Si—OH after hydrolyzing was used in the preparation of epoxy/SiO<sub>2</sub> composites. A stationary bonding phase was formed between C<sub>9</sub>H<sub>22</sub>O<sub>3</sub>SSi (KH580) and epoxy resin, which provides a good interfacial adhesion.

SiO<sub>2</sub>/epoxy, epichlorohydrin (40 mL), and benzyltrimethylammoniumchloride (C<sub>10</sub>H<sub>16</sub>NCl) (0.12 g) was prepared in a 250-mL, 3-neck, round-bottomed flask. The solution was stirred magnetically for 30 min at 70°C until the bisphenol A was completely dissolved in the solution. NaOH (6 mL, 28.57 wt %) solution was then added 1 drop per second. The reaction mixture was stirred at 60°C for 1 h. After that, atmospheric and vacuum distillation was carried out to remove unreacted epichlorohydrin. After distilling for 30 min, NaOH solution was added (4 mL, 28.57 wt %, and stirring was continued for 1 h) at 60°C. The prescribed amount of KH580, which was diluted with pure ethanol, was added into the mixture in terms of 1 drop per second under intensive stirring for 30 min. After reacting about 30 min, benzene was added (50 mL, and stirring was continued for 1 h) at 55°C. Thus the reaction product and other unreacted organics could be dissolved in the benzene. The extraction was then carried out by using warm water to recycle the organic solution. After that, the organic solution was refined by atmospheric and vacuum distillation until the yellowish product was obtained in the flask. Finally, the modified epoxy/SiO<sub>2</sub> composites were

**TABLE I**  
Reaction Composition and Silica Content of the  
SiO<sub>2</sub>/Epoxy System

Sample Number	Reaction Composition (g)			Silica Content (wt %)
	Bisphenol A	Epichlorohydrin (mL)	KH580	
EP	14.41	40	0	0
EP-S1	14.41	40	0.62	1
EP-S2	14.41	40	1.26	2
EP-S3	14.41	40	1.91	3
EP-S4	14.41	40	3.24	5
EP-S5	14.41	40	4.64	7

synthesized. The detailed experimental procedures and reaction compositions are given as Table I.

### Preparation of samples for shear strength

The curing agent (KH560) was added to the epoxy/SiO<sub>2</sub> composite by a stoichiometric ratio and agitated homogeneously. The adhesive was then coated on the steel plates until the coating was thin and bubbleless. The testing sample was made, as in Figure 1. The samples were first cured at 130°C for 4 h, then finally cured at 150°C for 2 h during each curing step.

In this research, the shear strength test was performed according to GB7124-86 equivalent with ISO 4587-1979. As shown in Figure 1, the dimensions of steel plates are 100 mm × 25 mm and the overlapping length is 12.5 mm. The two top arrows indicate the directions of the shearing. The shearing strength was tested by a universal testing machine.

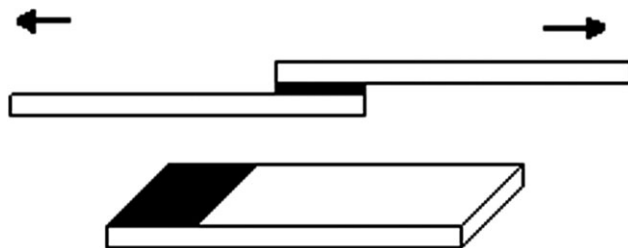
### Characterization methods

#### Fourier transform infrared analyses

The infrared (IR) absorption spectra of the samples were performed on an FTIR VERTEX 70 spectrometer using the KBr-pellet method.

#### Scanning electron microscopy

To study the morphology of modified epoxy resin, fractured surfaces obtained from shear adhesive



**Figure 1** The sample for testing of shear strength.

tests were coated with gold. Scanning electron micrograph was performed on a PHILIPS Quanta 200 environmental scanning electron microscope (ESEM).

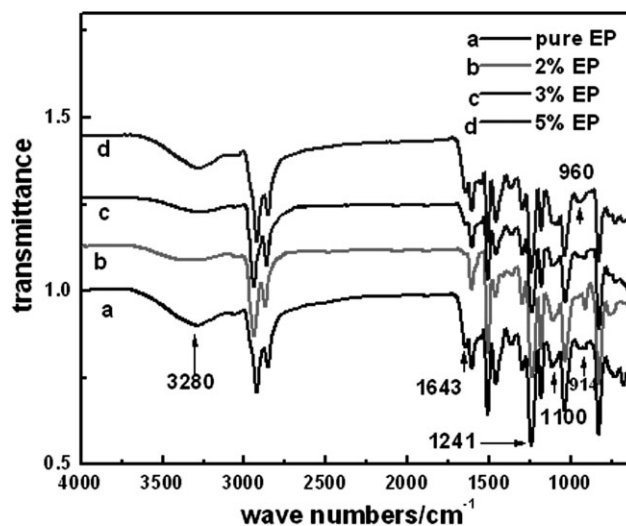
### Shear strength tests

The tensile shear strength of the epoxy resins was evaluated using the test machine WDW3200 universal tester. Results of shear strength were mean value among five tested specimens.

## RESULTS AND DISCUSSION

### Fourier transform infrared analyses

In Figure 2, the absorption at 1100 cm<sup>-1</sup> are attributed to dissymmetry flexible vibration<sup>13</sup> of C—O—C in pure EP, and the wide absorption at 3280 cm<sup>-1</sup> indicates the abundance of —OH on the surface of the KH580 and EP. As the content of the SiO<sub>2</sub> increased from 0 to 5%, the absorptions of epoxy resin-based composites at 1000 to 1100 cm<sup>-1</sup>, representing the dissymmetry flexible vibration of linear Si—O—C, are obviously wider compared with that of pure EP. Meanwhile, the absorption of epoxy resin-based composite at 3280 cm<sup>-1</sup>, representing the abundance of —OH, become much lower as compared with that of pure EP, which may imply that the silanol group Si—OH in the KH580 has reacted with —OH of EP to create a new covalent bonding Si—O—C. The reason for wider absorption between 1000 to 1100 cm<sup>-1</sup> is that the symmetric Si—O—Si stretching peak at 1030 to 1100 cm<sup>-1</sup>, C—O peak, and the new Si—O—C peak overlapped together. As the content of the SiO<sub>2</sub> increase, the absorption at



**Figure 2** IR spectra of epoxy resin, epoxy resin-based composite containing 2 wt %, 3 wt %, and 5 wt % SiO<sub>2</sub>/EP.

**TABLE II**  
Effects of KH580 Contents on Properties of the Adhesives

SiO <sub>2</sub> Content (%)	Shearing Strength (MPa)	Elongation (%)
0	10.24	3.20
1	16.62	13.6
2	18.40	13.5
3	20.86	14.0
5	24.78	20.75
7	17.79	10.65

1241 cm<sup>-1</sup> and 914 cm<sup>-1</sup>, representing the epoxy ring, become weaker, corresponding to the increased silica content, which means the reaction occurred between the epoxy ring and the silanol group Si—OH.

### Shear strength and SEM analysis

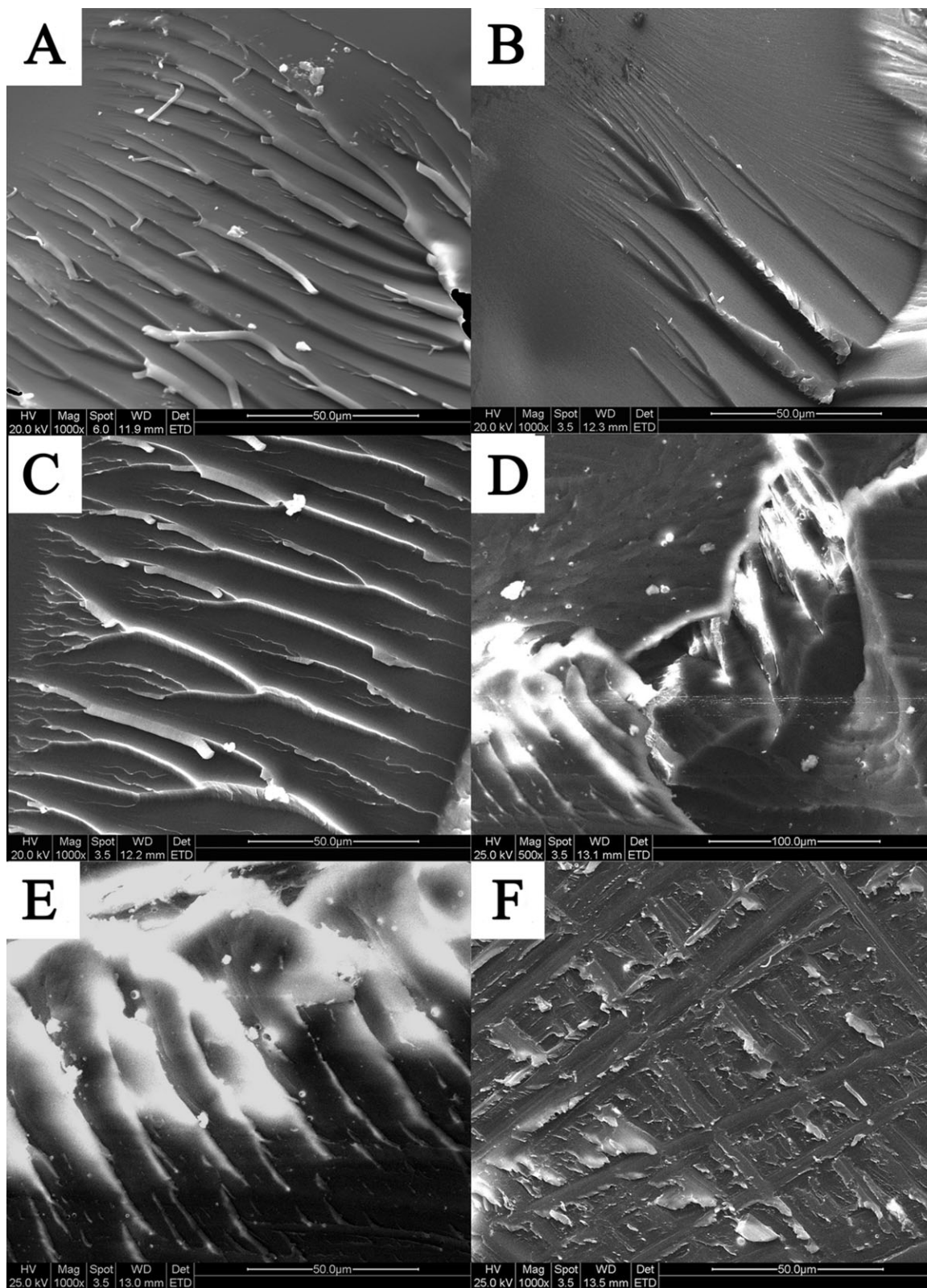
As shown in Table II, the shear strength of pure epoxy resin is 10.24 MPa. The shear strength of epoxy resin-based composite increases with increasing content of SiO<sub>2</sub> particles; optimal shear strength is 24.78 MPa when the content of SiO<sub>2</sub> reached 5 wt %; a decrease in the shear strength is observed when the content of SiO<sub>2</sub> is above optimal. At the same time, when the content of SiO<sub>2</sub> is below 5%, with the increase of the SiO<sub>2</sub> content, the elongation increases dramatically; when the SiO<sub>2</sub> content is above 5%, the elongation decrease significantly. Therefore, the optimal content of SiO<sub>2</sub> is 5% within the range of this research, and compared with the pure epoxy resin, the shear strength has increased by 142%. Ma et al.<sup>14</sup> adopted the liquor-mix method. The steady suspension was obtained through nano-SiO<sub>2</sub> surface modification and adhesive compounding. After the modification, the conclusion was that the optimal value of shearing strength is 17.991 MPa with the 2% content of SiO<sub>2</sub>. Compared with the pure epoxy resin of which the shear strength is 15.659 MPa, the shear strength increased by 14.89%. Therefore, a better improvement in shear strength was obtained after introducing KH580.

Toughening of resins with fillers could be explained by the role of crack joined by particles, depriving, curving river lines, micro-cracks, etc.<sup>15</sup> The fracture surfaces of the composites were observed using SEM. Figure 3(A–F) displays some representative SEM images of the fracture surfaces of the shear samples. Figure 3(A) shows that the surfaces of the pure epoxy samples were smooth and featureless and have much plane between the river lines and straight lines on fracture surfaces, representing brittle failure of homogenous materials. As shown in Figure 3(B,C), SEM images for the

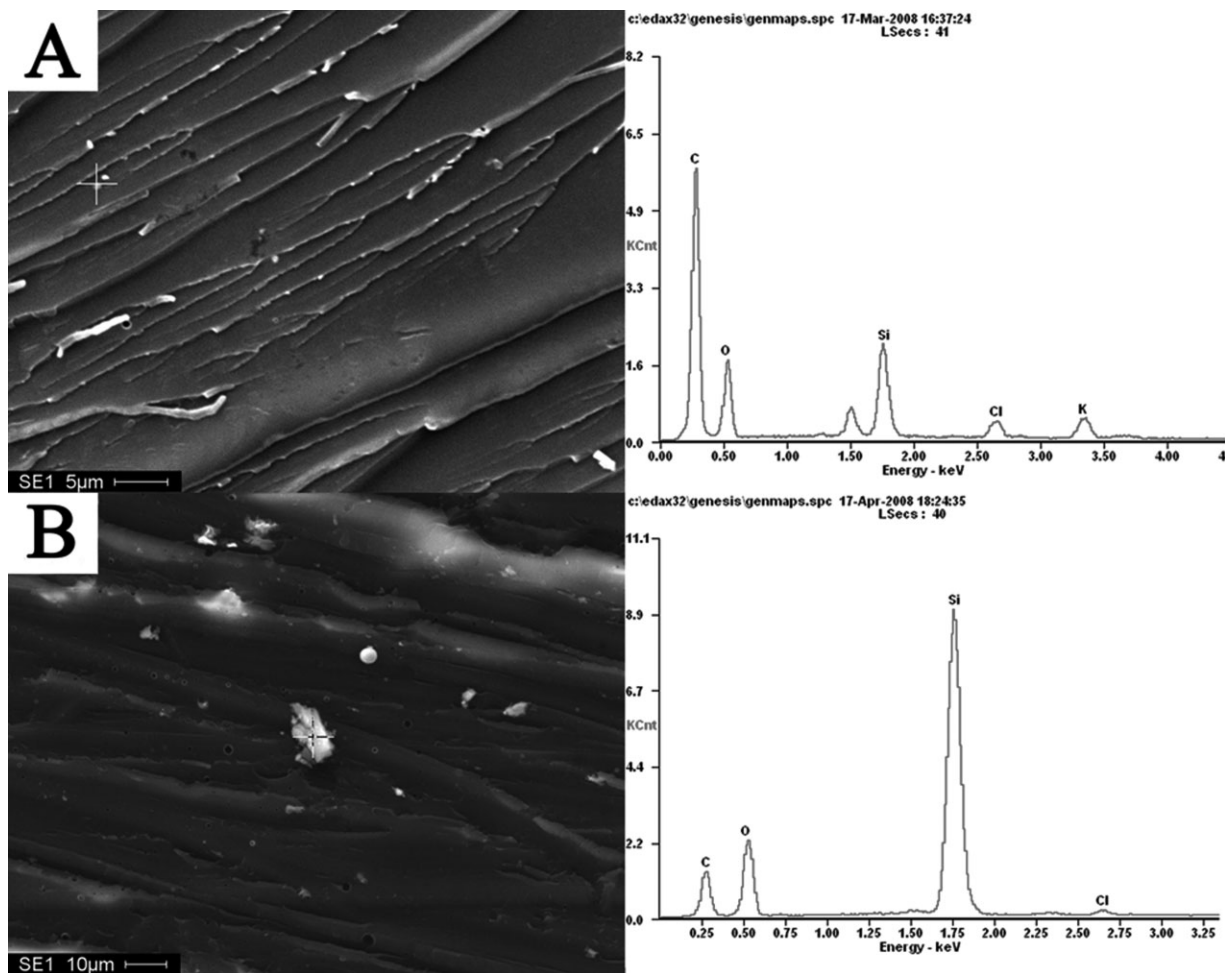
SiO<sub>2</sub>/epoxy composite samples with 2 wt % and 3% SiO<sub>2</sub> content, the fracture surfaces were significantly different from those of pure epoxy samples. The fracture surfaces were broken into small and rough fracture pieces, and many micro-cracks, plastic deformation, and divergent and sinuous river lines can be seen on rough fracture surfaces contributing to improvement of the toughness of the composite. Parallel river lines are shown on fracture surfaces in Figure 3(D,E); however, markedly plastic deformation and some holes with rough edges revealed the role of depriving SiO<sub>2</sub> particles. Micro-cracks as dendritical structures are shown on the center part of Figure 3(E). More energy was absorbed by improving resistance to crack expansion and plastic formation such as cavitations, micro-cracks, and shearing caused by the bonded stationary phase between SiO<sub>2</sub> and epoxy resin. However, the improved toughness by the rough fracture surfaces would be overwhelmed by the effect of aggregated SiO<sub>2</sub> particles, resulting in a reduced toughness and adhesive strength. It was noticed that toughness of SiO<sub>2</sub>/epoxy resin-based composite would fall for agglomeration of SiO<sub>2</sub> above the optimal content of SiO<sub>2</sub>. However, Epoxy resin-based composite containing 5 wt % SiO<sub>2</sub> exhibits the highest toughness; see Figure 3(D).

### Energy dispersive spectrometer analysis

The ESEM was applied to observe the morphology of the epoxy resin-based composite. Figure 4 displays the energy dispersive spectrometer (EDS) photograph that can be used to confirm the particle aggregation of the KH580 structure. The EDS photograph of the cross mark demonstrated high Si intensity. We confirmed the particle aggregation in epoxy resin-based composite to be a KH580 aggregation, since KH580 contained Si element in the epoxy resin-based composite. On the other hand, we can see that the morphology of KH580 aggregation is becoming more and more remarkable as the content of KH580 increases. The particulates disperse as individual particles, which results in satisfactory properties. When the content of the SiO<sub>2</sub> is above 5%, these particulates can only act as filler, and the concentration of local stress probably reduces the system's performance. The KH580's modification mechanism is that the SiO<sub>2</sub> particulates that disperse in the epoxy resins act as a stress concentrated body. They not only can induct the silver crack and shearing band to absorb energy but also can terminate the silver crack. When the particulates fall out from the surface of the epoxy resin, they can release the elastic stress energy of the matrix, and then they make the material toughen. There is a best distance between the SiO<sub>2</sub> particulates, which corresponds to proper modifier content. Therefore, the presence of



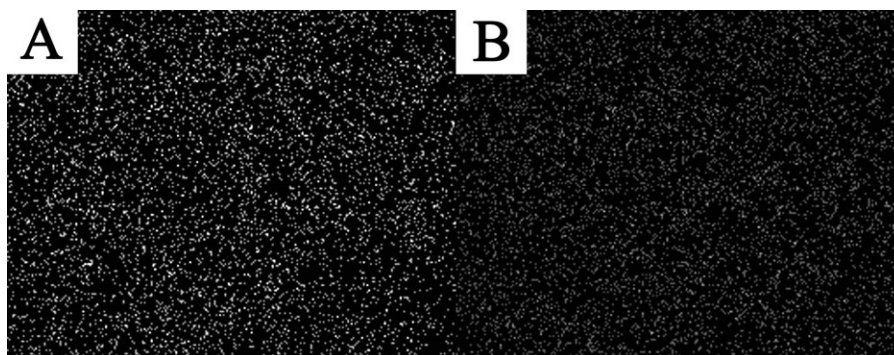
**Figure 3** SEM images of fractured surfaces of epoxy resin (A) and epoxy resin-based composites containing 2 wt % (B), 3 wt % (C), 5 wt % (D, E), and 7 wt % (F) SiO<sub>2</sub> particles. Image E is a part of image D.



**Figure 4** The EDS spectrum and SEM micrograph of epoxy resin-based composite (A) EDS spectra of 5% SiO<sub>2</sub>/EP and (B) EDS spectra of 7% SiO<sub>2</sub>/EP.

SiO<sub>2</sub> particles might cause perturbations along the crack front, thus altering the path of the propagating crack. The fracture toughness was then improved by incorporating SiO<sub>2</sub> into the epoxy composites. In addition, from the difference between Figure 4(A) and (B), we concluded that the composites with 5% SiO<sub>2</sub> afforded optimal toughness.

Figure 5 displays the distribution of the S and Si elements in a certain region of the hybrid material. Figure 5(A,B) displays the distribution of S and Si element, respectively. We can confirm that it is the result of the reaction of KH580 and the epoxy resin, since the EDS photograph demonstrated homogeneous distribution of S and Si elements at the



**Figure 5** EDS images showing the distribution of elements in the hybrid material (A) distribution of S element and (B) distribution of Si element.

same area. On the other hand, the image shows that the distribution of S and Si is approximately the same from which we can confirm the Si element belonged to KH580, since only in KH580 the Si and S elements exist together. Therefore, we found that the KH580 adopts two forms in the hybrid material. Some KH580 aggregated with each other to form particles; the other KH580 reacted with epoxy resin without any aggregation.

### CONCLUSIONS

These studies on the fracture surfaces and mechanical properties show that the introduction of KH580 into epoxy resin has dramatic effects on composites. Shear strength tests showed that both the shear strength and elongation of epoxy resin-based composite increased and then decreased after SiO<sub>2</sub> content reached 5 wt %, optimal value was 24.78 MPa. Existence of particles is crucial to the morphological structure of composites, which in turn affects the shear strength and the toughness of the composites. More interfacial surfaces can be generated between polymer and particles, which assists in absorbing the stress.

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