

# In Situ Synthesis and Characterization of ZnS/Epoxy Nanocomposites via Gas-Liquid State Reaction Method

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**ABSTRACT:** In this article, the ZnS/epoxy nanocomposites were successfully prepared by the reaction of zinc acetate and H<sub>2</sub>S gas via a simple step. Epoxy resin acted as the matrix for the formation of ZnS nanoparticles (10–20 nm) in the reaction system and kept them from agglomerating. The structure, composition, and mechanical properties of the resultant products were successfully investigated by powder X-ray diffraction, transmission electron microscope, field emission scanning electron microscope, energy dispersive X-ray fluorescence, and universal testing machine. Meanwhile, by employing differential scanning calorimetry (DSC)

we had studied, under nonisothermal condition, the kinetic analysis of the cure reaction which was performed using two classic models: Kissinger and Flynn-Wall-Ozawa. The activation energy of curing reaction was 74.63 kJ/mol and 77.57 kJ/mol, respectively, by Kissinger's and Flynn-Wall-Ozawa's methods. The possible mechanism of preparation of ZnS/epoxy composites was discussed in this article. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1426–1430, 2012

**Key words:** composites; kinetics; mechanical properties; thermosets

## INTRODUCTION

Over the last decade, academic and industrial scientists have become increasingly interested in modifying the properties of epoxy resin by adding nanoscale fillers to enhance their mechanical, optical, thermal, and abrasive performance.<sup>1–8</sup> Therein, metal sulfide (such as ZnS, CdS, PbS, MnS, and CoS) nanomaterials have been the focus of considerable interest due to their unique optical, magnetic, catalytic, and electrical properties.<sup>9–12</sup> Therefore, it is important to prepare metal sulfide/epoxy composites with easy processabilities. However, ability to control good dispersion of nanocrystals in polymers is one of the key challenges that has to be overcome for achieving optimal performance of these organic/inorganic hybrids. Fortunately, *in situ* synthesis of inorganic nanocrystals in polymers has been widely studied,<sup>13–15</sup> which could successfully improve the dispersion of inorganic nanocrystals into organic polymers for better performance than direct melt mixing.

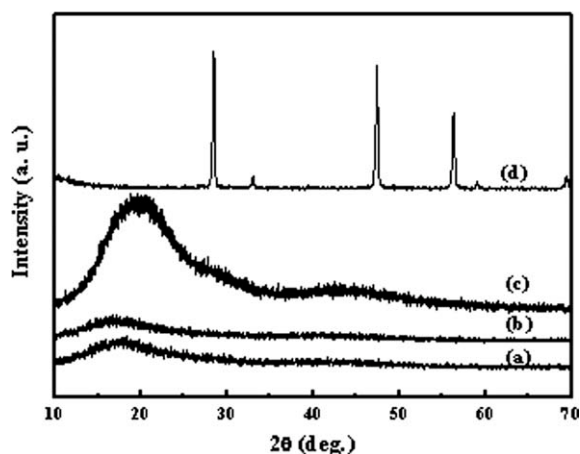
*In situ* synthesis is an important method to prepare nanoscale particles with good dispersion in the polymer matrix. Pan et al.<sup>16</sup> reported that *in situ* synthesis of PbS/epoxy was achieved by the reaction of lead acetate and sodium sulfide, but the aftertreat-

ment of the product by vacuum filtration and repeated washing with water was extremely inconvenient. Lin et al.<sup>17</sup> successfully prepared nanosized magnetite particles *in situ* within poly(vinyl alcohol) solutions by precipitating Fe<sup>2+</sup> ions or a mixture of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions with NaOH solution. Wu et al.<sup>18</sup> demonstrated that the composite particles of nano calcium carbonate/polymethyl methacrylate were prepared by soapless emulsion polymerization technique in the aqueous suspension of nano calcium carbonate. Wang et al.<sup>19</sup> demonstrate that the nano-ZnO particles modified by the silane-coupling agent can enhance the mechanical properties and the thermal conductivity.

More and more researchers devoted themselves to improve the properties of the polymer by ZnS particles.<sup>11–12,20</sup> Liu et al.<sup>11</sup> prepared the inorganic-organic crosslinking polythiourethane/ZnS nanocomposites with high refractive index and transmittance and found that the refractive index of the highly transparent nanocomposite films linearly increased from 1.643 to 1.792 with the increase of the ZnS content. Xu et al.<sup>12</sup> reported that the resultant Poly(*o*-methyl-acrylamideyl-benzoic acid)-ZnS nanocomposites displayed good film formability and the films also showed two emissions at 370 and 425 nm. Zhou et al.<sup>19</sup> stated a new synthetic route to hybridize ZnS semiconductor nanoparticles and poly(vinyl alcohol)-based electrospinning nanofibers.

However, to the authors' knowledge, no work has been reported on the mechanical property and

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**Figure 1** XRD patterns of (a) neat epoxy after curing, ZnS/epoxy (b) after curing and (c) before curing, (d) ZnS nanoparticles.

thermal stability of epoxy via *in situ* synthesis of ZnS nanocrystals in epoxy resin matrices at gas-liquid interface. The main purpose of this work was to develop new ZnS/epoxy materials via *in situ* synthesis method that can be used in the manufacture of surface coatings and electronic equipment. It is significant that the ZnS/epoxy composites are prepared without using any additives avoiding troublesome aftertreatment compared with other synthesis methods.

## EXPERIMENTAL

### Materials

Transparent epoxy resin (YN1828) was purchased from Jiangsu Kumho Yangnong Chemical of China. The curing agent Methyl hexahydrophthalic anhydride (Me-HHPA, Specification: SHY9603) was supplied from Qingyang Chemistry of China. The accelerant benzyldimethylamine,  $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{S}$ ,  $\text{H}_2\text{SO}_4$ , methanol, and acetone were analytical reagents and offered from Sinopharm Chemical Reagent of China. Sulfureted hydrogen ( $\text{H}_2\text{S}$ ) was prepared by the reaction of  $\text{Na}_2\text{S}$  and  $\text{H}_2\text{SO}_4$  aqueous solution in our lab.

### *In situ* preparation of ZnS/epoxy nanocomposites

$\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$  (0.02 mol) was dissolved in 60 mL methanol, and 200 g YN1828 and 150 mL acetone were added into the above solution with vigorous agitation at  $20^\circ\text{C}$  to form transparent solution. Sulfureted hydrogen ( $\text{H}_2\text{S}$ ) was prepared by the reaction of 15.61 g  $\text{Na}_2\text{S}$  particles and adequate 10 wt %  $\text{H}_2\text{SO}_4$  aqueous solution in our laboratory. Then, the pure and stable gas  $\text{H}_2\text{S}$  (about 0.2 mol) was added into the above resin solution for about 1.5 h, and system quickly became opaque due to the very low solubility product of ZnS (about  $10^{-23}$ ), after that kept stirring at  $20^\circ\text{C}$  for 3 h. Subsequently, the prod-

uct was thermally treated at  $140^\circ\text{C}$  for 2 h in a vacuum system under the pressure of  $-0.1$  MPa to remove dissolvent, acetic acid and redundant  $\text{H}_2\text{S}$ . Finally, pale yellow ZnS/epoxy hybrid was successfully obtained.

### Sample preparation

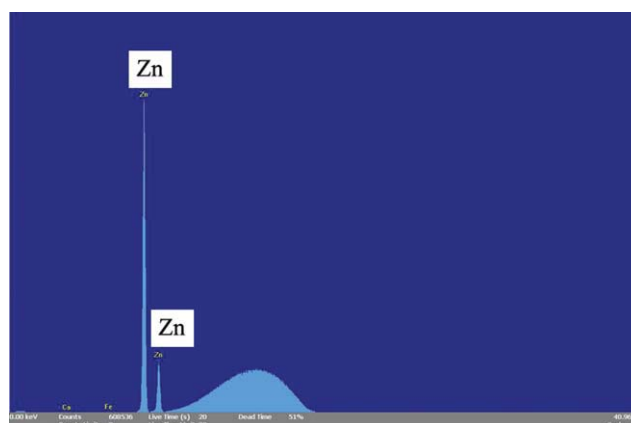
The resulting ZnS/epoxy hybrid, curing agent and accelerant (the weight ratio is 1 : 1 : 0.015) were well stirred until a homogeneous mixture and treated in a vacuum system under the pressure of  $-0.1$  MPa to remove bubbles. The mixture was poured into a self-manufacture polytetrafluoroethylene mold and heated in an oven for 1 h at  $80^\circ\text{C}$  and 2 h at  $120^\circ\text{C}$ . After this curing process, the samples with a thickness of 4 mm were easily removed from the molds.

### Characterization of the products

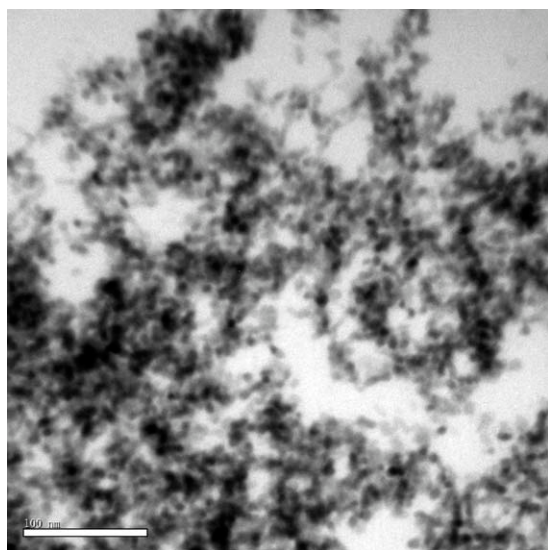
The obtained products were characterized by X-ray diffraction (XRD) (German Bruker AXS D8 ADVANCE X-ray diffractometer), transmission electron microscope (TEM) (The Netherlands Philips Tecnai-12 microscope), field emission scanning electron microscope (Japan Hitachi S-4800 FESEM), energy dispersive X-ray fluorescence (Thermo Scientific ARL QUANT'X EDXRF Spectrometer), and DSC (Germany Netzsch DSC 204 F1). Tensile testing was carried out on dumbbell-shaped samples (ISO 527/2) using a universal testing machine "WDW-5 (Shanghai hualong test instructions)." The measurements were all carried out at  $23 \pm 1^\circ\text{C}$  using a rate of 2.0 mm/min.

## RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the neat epoxy, ZnS/epoxy after curing and ZnS nanoparticles



**Figure 2** EDXRF spectrum of ZnS/epoxy composites after curing. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com)]

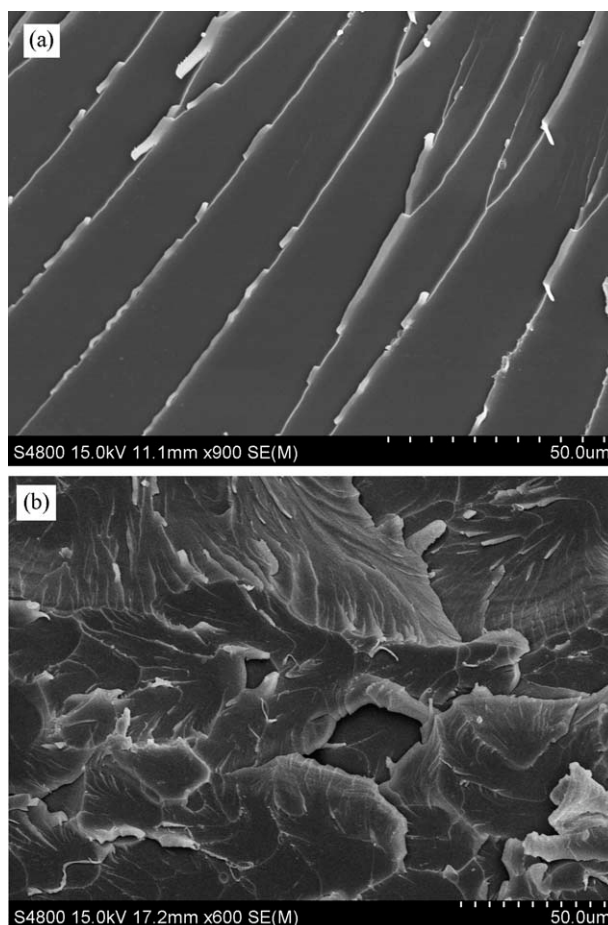


**Figure 3** TEM picture of ZnS/epoxy composites after curing.

obtained by washing of the ZnS/epoxy hybrid before curing with adequate acetone to remove epoxy. A very broad peak at around  $20^\circ$  is observed due to the amorphous nature of the epoxy resin in Figure 1(a). As shown in Figure 1(b,c), the significant peak of ZnS becomes weak due to the existence of epoxy resin on the surface of the ZnS particles and the little weight content via *in situ* synthesis method. We can find that ZnS prepared by washing of the ZnS/epoxy hybrid is cubic phase (JCPDS card no. 03-065-1691) in Figure 1(d), whose sizes are about 0.62 nm calculated from the half-width of its XRD peaks according to the well-known Debye-Scherrer formula.<sup>21</sup> It demonstrates that the ZnS/epoxy composites can be prepared via *in situ* synthesis method in the epoxy matrices.

Meanwhile, the element content of the ZnS/epoxy after curing is investigated by EDXRF, the result of quantitative analysis shows that the mole ratio of Zn and S is 1.07 : 1, as shown in Figure 2. Besides, the EDXRF analysis further confirms the result of the XRD pattern of the ZnS/epoxy composites in Figure 1.

TEM is a straightforward technique to visualize the dispersion quality of particles with epoxy. TEM image of toughened epoxy resin is shown in Figure 2. A homogenous distribution of particles is visible and the average size of ZnS particles is about 10–20



**Figure 4** FESEM micrographs of fracture surfaces of (a) neat epoxy, (b) ZnS/epoxy composites after curing.

nm, although some small agglomerates remain present in the epoxy matrix.

FESEM micrographs of fracture surfaces of untoughened and toughened epoxy resin are shown in Figure 3. Figure 3(a) shows the unmodified epoxy after tensile testing in which a smooth fracture surface as well as cracks in different planes can be seen. This is an indication of a brittle fracture of the unmodified epoxy. It indicates that a relatively small amount of energy was consumed to fracture the specimens. Figure 3(b) shows the fracture surface of the modified epoxy after tensile testing. It depicts rougher features such as stress whitened zones and out-of-plane flaking markings which normally exploit additional strain energy to be formed during the deformation process of the specimens.

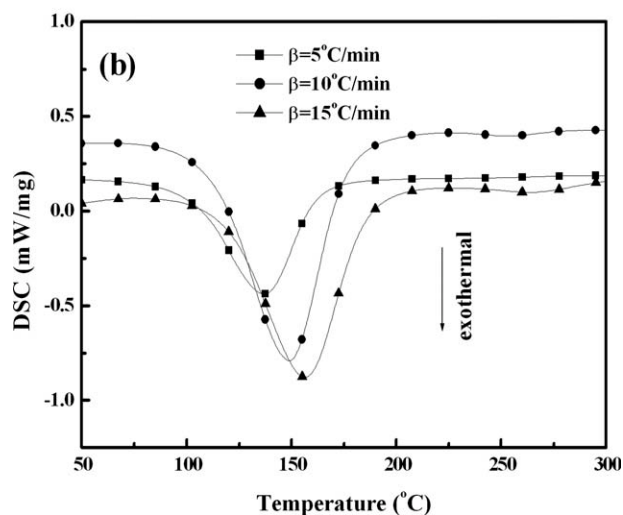
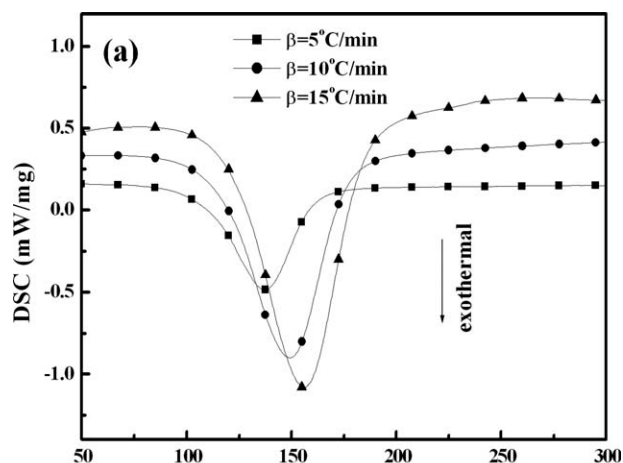
**TABLE I**  
The Mechanical Property and Activation Energies of Neat Epoxy and ZnS/Epoxy

Sample	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)	Kissinger (kJ/mol)	Flynn-Wall-Ozawa (kJ/mol)
Neat epoxy	26.36 ± 2.34	8.59 ± 0.65	0.26 ± 0.03	78.85 ± 1.47	81.58 ± 1.44
ZnS/epoxy	39.5 ± 2.69	9.75 ± 0.74	0.37 ± 0.03	74.63 ± 0.36	77.57 ± 0.38

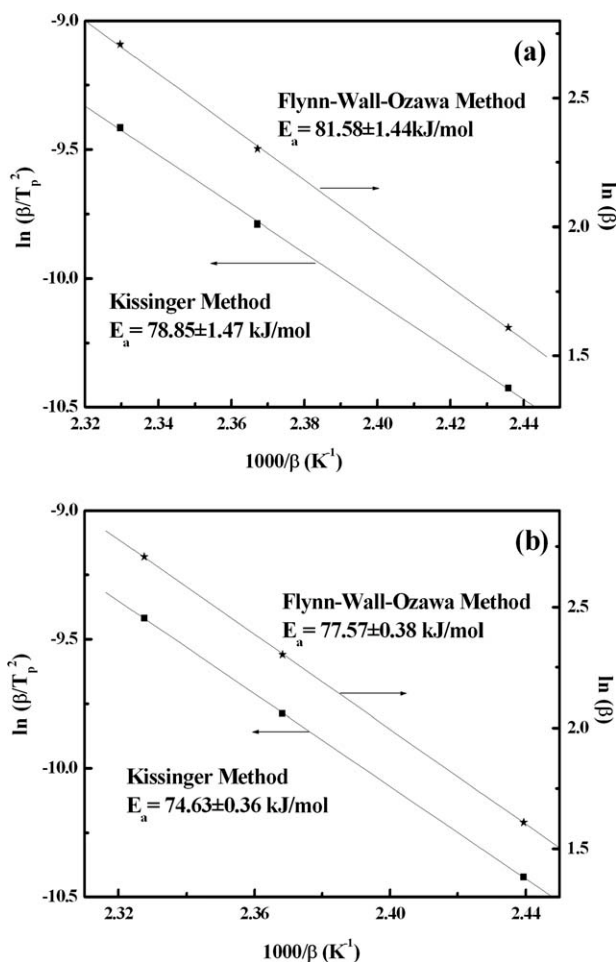
Table I shows the tensile test of neat epoxy and ZnS/epoxy nanocomposites after curing. After introducing ZnS nanoparticles, all mechanical properties have been significantly enhanced compared to the sample S1. The improvement of ultimate tensile stress, elongation at break and tensile modulus achieved is about 49.85%, 13.5%, and 42.31% as shown in Table I, respectively.

The neat epoxy and ZnS/epoxy are cured at different isothermal temperatures (the heating rate is 5, 10, 15°C/min, respectively), as shown in Figure 4. Kinetic analysis is performed using later kinetic models expressed as eq. (1) and (2): Kissinger and Flynn-Wall-Ozawa methods,<sup>22–26</sup> that are used by their wide applicability in comparison with other nonisothermal methods.

$$\text{Kissinger} : \frac{d[\ln(\beta/T_p)^2]}{d[1/T_p]} = -\frac{E_a}{R} \quad (1)$$



**Figure 5** Heat flow measured of (a) neat epoxy and (b) ZnS/epoxy by DSC during cure at different rates: 5, 10, 15°C/min.



**Figure 6** Activation energies of (a) neat epoxy and (b) ZnS/epoxy obtained by Flynn-Wall-Ozawa and Kissinger methods.

$$\text{Flynn-Wall-Ozawa} : \frac{d[\ln\beta]}{d(1/T_p)} = -\frac{1.052E_a}{R} \quad (2)$$

where  $E_a$  is the activation energy of curing,  $R$  is the ideal gas constant,  $\beta$  is the heating rate,  $T_p$  is the maximal temperature of exothermic peak.

Applying the Kissinger and Flynn-Wall-Ozawa methods to the maximum reaction rates (peaks of DSC thermogram as shown in Fig. 4), the activation energies are determined by the slopes of the lines in Figure 5, and these values are summarized in Table I (Fig. 6). It can be seen that the values obtained by the Flynn-Wall-Ozawa method are slightly higher than the values obtained by the Kissinger method for the neat epoxy and ZnS/epoxy, but these values are very similar. Moreover, the activation energy of ZnS/epoxy is lower than the neat epoxy calculated by whichever method.

The reason of successful preparation of ZnS/epoxy nanocomposites by above-mentioned procedure is simple to understand. Due to the nice intersolubility of zinc acetate, methanol, acetone, and

epoxy resin with vigorous agitation at 20°C (the viscosity of YN1828 is about 11000 mPa s), a homogeneous and transparent solution can be easily obtained. When excess H<sub>2</sub>S is slowly added into the above solution, the ZnS nanoparticles are quickly formed at the gas-liquid interface via the reactions between Zn<sup>2+</sup> and H<sub>2</sub>S due to the very low solubility product of ZnS.<sup>27,28</sup> Meanwhile, high viscosity of epoxy resin plays an essential role in the *in situ* formation of ZnS nanoparticles, and keeps the nanoparticles well dispersed and preventing separation.<sup>16,29</sup> The relational reaction described as follow:



### CONCLUSIONS

In this article, the mechanical properties and activation energy of ZnS/epoxy nanocomposites were investigated. The results showed that the epoxy resin modified by ZnS nanoparticles (about 10–20 nm) had significant improvement compared to neat epoxy. This preparation technology suggests a simple and controllable route to synthesize metal sulfide/polymer composites in different applied regions.

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