

Preparation and Optical Properties of Transparent Epoxy Composites Containing ZnO Nanoparticles

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ABSTRACT: Polymer nanocomposites are usually made by incorporating dried nanoparticles into polymer matrices. This way not only leads to easy aggregation of nanoparticles but also readily brings about opaqueness for nanocomposites based on functionally transparent polymers. In this letter, transparent ZnO/epoxy nanocomposites with high-UV shielding efficiency were prepared via two simple steps: first, *in situ* preparation of zinc hydroxide (Zn(OH)₂)/epoxy from the reaction of aqueous zinc acetate (Zn(Ac)₂·2H₂O) and sodium hydroxide (NaOH) at 30°C in the presence of high-viscosity epoxy resin; second, thermal treatment of the as-prepared Zn(OH)₂/epoxy hybrid into ZnO/epoxy composites. Optical properties of

the resultant ZnO/epoxy nanocomposites were studied using an ultraviolet-visible (UV-vis) spectrophotometer. The nanocomposites containing a very low content of ZnO nanoparticles (0.06 wt %) possessed the optimal optical properties, namely high-visible light transparency and high-UV light shielding efficiency. Consequently, the as-prepared ZnO/epoxy nanocomposites are promising for use as novel packaging materials in lighting emitting diodes technology. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: composites; UV-vis spectroscopy; X-ray; thermosets

INTRODUCTION

The packaging materials for solid state lighting emitting diodes (LEDs) need possess high-visible light (>400 nm) transparency and yet high-ultraviolet (UV) light (<400 nm) resistance. However, the severe yellowing of epoxy encapsulant would occur due to junction heat and short-wavelength emission,^{1,2} which would significantly reduce the lifetime of LEDs. Extensive research effort has been devoted to prepare high-UV light resistance of packaging materials via structural design of transparent epoxies, or addition of organic and inorganic UV light absorbents.^{3,4} Huang et al.⁵ reported that the silicone-epoxy composites have excellent UV resistance in the presence of aluminum complex/silanol compound catalysts. Yang et al.⁶ found that the highly transparent ZnO quantum dots (ZnO-QDs)/epoxy nanocomposites, which can emit intense luminescence were prepared by uniformly dispersing

ZnO quantum dots in a transparent epoxy resin via a direct dispersion method. Sun et al.⁷ indicated exfoliated zirconium phosphate nanoplatelets instead of organic capping agents, it can well control the state of dispersion of ZnO quantum dots in epoxy matrix.

To date, more and more researchers pay attention to prepare ZnO nanomaterials because of their potential applications in numerous areas such as catalyst, electronics, gas sensors, etc.^{8–13} And many methods have been proposed to synthesize ZnO nanocrystals such as aqueous solution deposition, vapor phase transport, electrochemical deposition, etc.^{14–19} Additionally, ZnO is an extremely inorganic high-UV-shielding material with low-refractive index and has been widely applied to polymers as UV-light filters.^{20–23} However, to our knowledge, no work has been reported on the photostability of epoxy-based nanocomposites as UV-LED encapsulating materials via *in situ* synthesis of ZnO nanocrystals in epoxy resin matrices.

Herein, we report the UV shield property of ZnO/epoxy composites containing a very low content on the basis of our previous research work.²⁴ Then the optical properties of the resultant ZnO/epoxy nanocomposites were studied by an ultraviolet-visible (UV-vis) spectrophotometer. In addition, the effects of particle size, dispersion and structure of ZnO/epoxy nanocomposites were also investigated.

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TABLE I
The Relational Information of the Synthesis and Characterization of the ZnO/Epoxy Composites

| Sample number | Raw materials | | Theoretic content | EDXRF analysis | UV-light shielding property |
|---------------|------------------|----------------------|--------------------|-------------------|-----------------------------|
| | Zinc acetate (g) | Sodium hydroxide (g) | ZnO content (wt %) | ZnO content (ppm) | Value at 370 nm (%) |
| S1 | 0 | 0 | 0 | 0 | 86.66 |
| S2 | 0.16 | 0.06 | 0.04 | 81.6 | 100 |
| S3 | 0.24 | 0.09 | 0.06 | 129.6 | 100 |
| S4 | 0.32 | 0.12 | 0.08 | 156.5 | 100 |
| S5 | 0.40 | 0.15 | 0.1 | 200.0 | 100 |

EXPERIMENTAL

Materials

Transparent epoxy resin (YN1828) was purchased from Jiangsu Kumho Yangnong Chemical Co. of China. The curing agent Methyl tetrahydrophthalic anhydride (Me-THPA, Specification: SHY9603) was supplied from Qingyang Chemistry Co. of China. The accelerant benzyldimethylamine (BDMA), Zn(Ac)₂·2H₂O and NaOH (they were all analytical grade) were obtained from Sinopharm Chemical Reagent Co. of China.

In situ preparation of Zn(OH)₂ in epoxy resin matrices²⁴

Two solutions were prepared as follows: solution A—Zn(Ac)₂·2H₂O was dissolved in 60 mL distilled water; and solution B—NaOH was also dissolved in 30 mL distilled water (molar ratio of NaOH and Zn(Ac)₂·2H₂O is 2 : 1), the weight of NaOH and Zn(Ac)₂·2H₂O was listed in the Table I. One hundred fifty grams of epoxy resin YN1828 and 60 mL solution A were added into 500 mL four-neck round-bottom flask and mixed with each other at 30°C for 30 min to form white stable emulsion. After that, solution B was slowly added into the above emulsion for about 20 min, then the white insoluble material Zn(OH)₂ was quickly formed due to its very low-solubility product (about 10⁻¹⁷),²⁵ afterward the emulsion was kept stirring at 30°C for 2 h. The as-prepared product was adequately washed with warm water to remove the by-product sodium acetate. Finally, Zn(OH)₂/epoxy hybrid was successfully obtained.

Preparation of ZnO/epoxy nanocomposites

ZnO/epoxy complex was prepared by thermal treatment of Zn(OH)₂/epoxy hybrid at 145–150°C for 2 h in a vacuum system under the pressure of -0.1 MPa to remove distilled water (the desolvation temperature is less than 150°C at Jiangsu Kumho Yangnong Chemical Co. of China) and completely decompose Zn(OH)₂ into ZnO (Zn(OH)₂ = ZnO + H₂O). The

resulting ZnO/epoxy hybrid, curing agent and accelerant (the weight ratio is 1 : 1 : 0.015) were well stirred to obtain a homogeneous mixture, then which was poured into a self-manufactured PTFE mould and heated in an oven for 1 h at 80°C and 2 h at 120°C. After this curing process, the samples with a thickness of 4 mm were easily removed from the mould. The filler content in uncured ZnO/epoxy is 0, 0.04, 0.06, 0.08, and 0.1 wt %, respectively, as shown in Table I.

Characterization of the products

Powder XRD patterns of the obtained products were recorded at a scanning rate of 8°/min in the 2θ range of 10–80°, using a Bruker D8 ADVANCE diffractometer system with a Cu K_α irradiation (λ = 1.5418 Å). Transmission electron microscopy (TEM) images were taken with a Philips Tecnai12 TEM at an accelerating voltage of 120.0 kV after sliced by Leica EM UC6. EDXRF spectra were tested by Thermo Scientific ARL QUANT'X EDXRF Spectrometer, UV-vis transmittance spectra were obtained on a Shimadzu UV-2550 spectrophotometer using ZnO/epoxy composites after curing with specimen dimensions equal to 4 ± 0.5 mm × 10 ± 0.5 mm cross-section and 80 ± 1 mm in length. The viscosity of YN1828 was obtained on Brookfield DV-II + pro viscosimeter according to testing standard ASTM D 445-2009.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction pattern of the composites with different contents after curing. A very broad peak at around 20° is observed due to the amorphous nature of the epoxy resin in Figure 1(S1). As shown in Figure 1(S2–S5), the significant peak of ZnO becomes weak due to the existence of epoxy resin on the surface of the ZnO particles and the little weight content via *in situ* synthesis method. When improving the content of ZnO to 5 wt %, the product in epoxy matrix after curing was hexagonal phase ZnO (JCPDS card no. 01-089-1397) as shown in Figure 1(a). It illustrates that Zn(OH)₂/epoxy

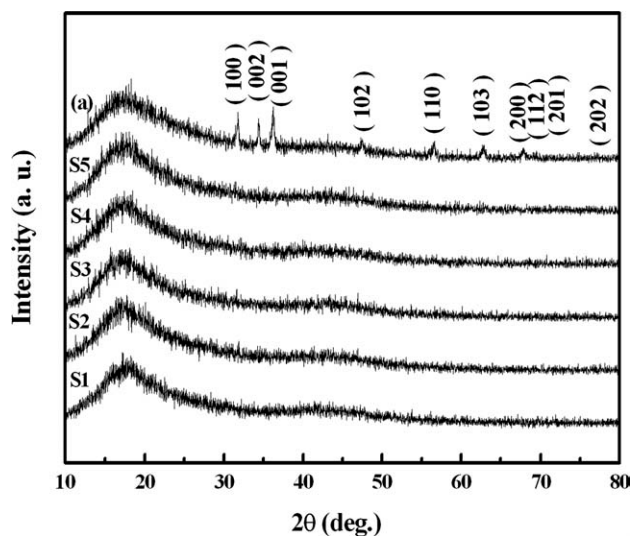


Figure 1 XRD patterns of (S1) neat epoxy, ZnO/epoxy (S2–S5) with different lower weight fractions, (a) with 5% higher-weight fractions.

hybrid can be easily prepared in the synthesis process because of its low-solubility product. In addition, no XRD peaks of Zn(OH)_2 are visible in

Figure 2 (S2–S5,a), suggesting that Zn(OH)_2 has been completely transformed into ZnO at 145–150°C under the current vacuum conditions.

Meanwhile, the element content of the ZnO/epoxy after curing is investigated by energy dispersive X-ray fluorescence (EDXRF) as shown in Table I and Figure 2. Although the results are not completely corresponding to the theoretic weight content due to the lower fraction on the surface of the ZnO/epoxy composite after curing. However, we can find that the presence of Zn element and increase regularly, which further confirms the result of the X-ray diffraction pattern of the ZnO/epoxy composites in Figure 1.

TEM is a straightforward technique to visualize the dispersion quality of particles with epoxy. TEM image of ZnO/epoxy composites is shown in Figure 3. A homogenous distribution of particles is visible and the average size of ZnO particles is about 10–20 nm, although some small agglomerates remain present in the epoxy matrix.

Figure 4 shows the UV–vis spectra of samples S1–S5 in transmittance mode with wavelengths ranging from 200 to 800 nm. The transmittance of S1

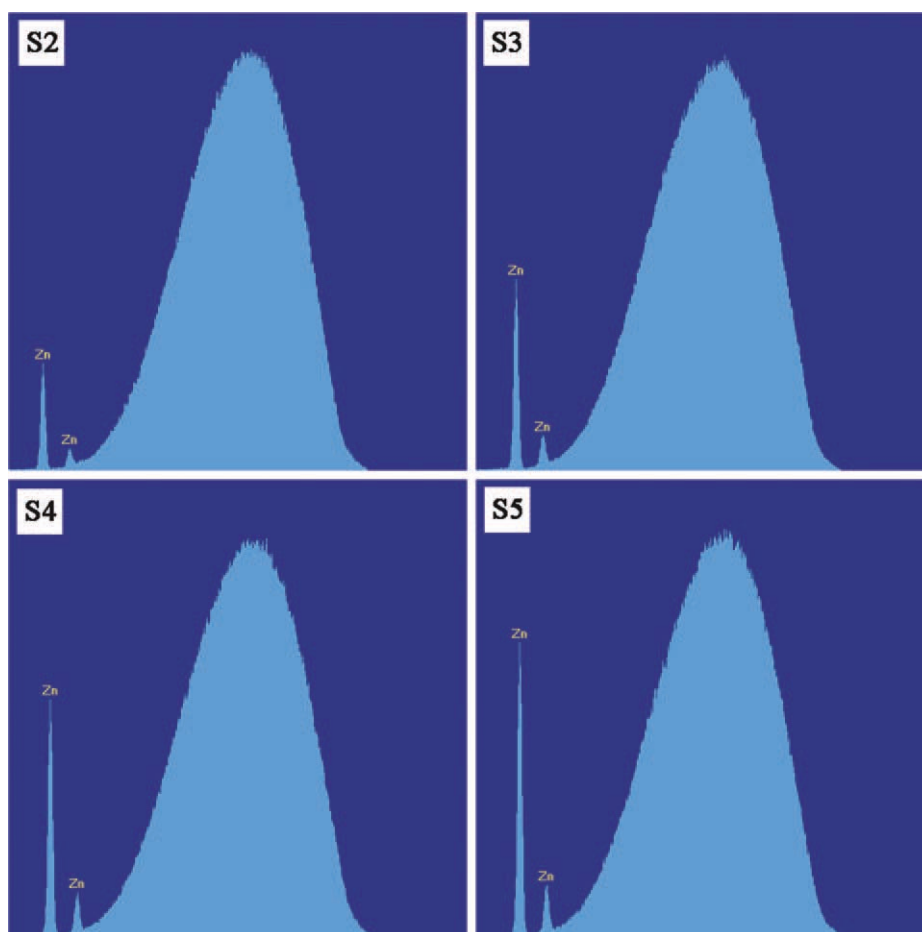


Figure 2 EDXRF spectrum of sample S2–S5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

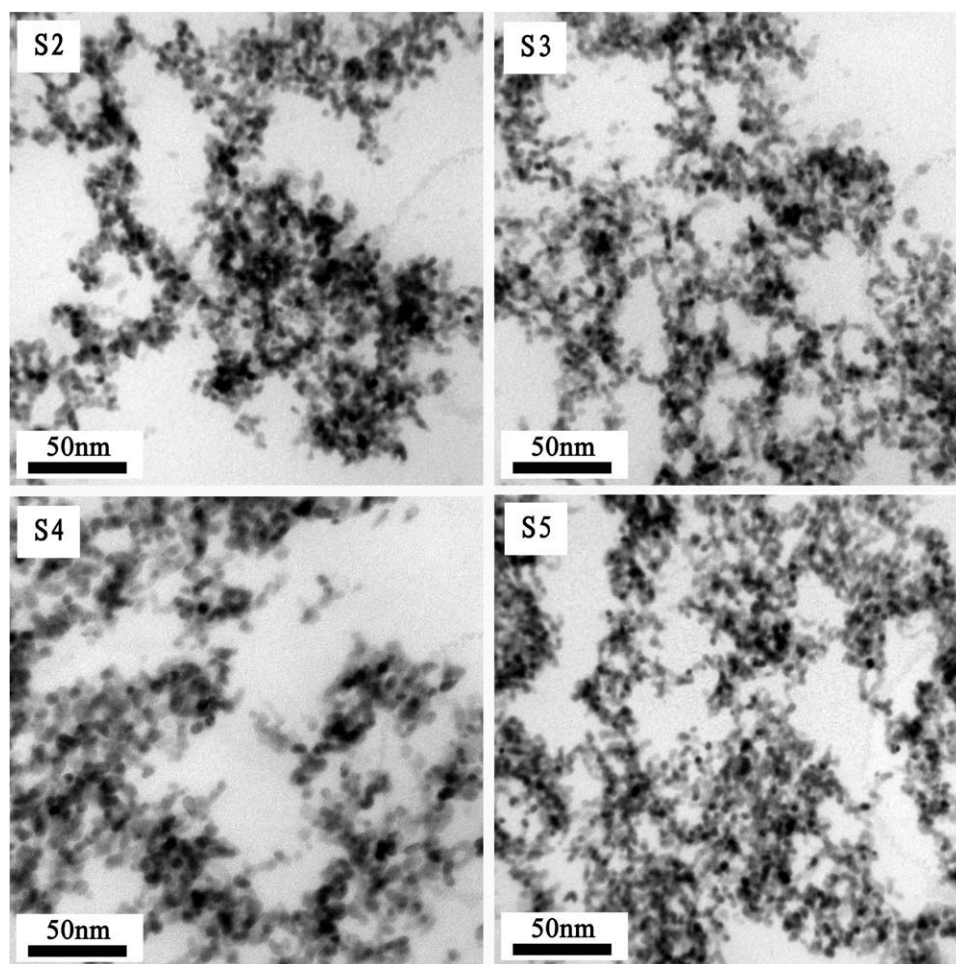


Figure 3 TEM pictures of ZnO/epoxy nanocomposites with different weight fractions.

having wavelengths above 309 nm increases with the wavelength and saturates at around 91% as the wavelength >700 nm. The relatively low transmittance

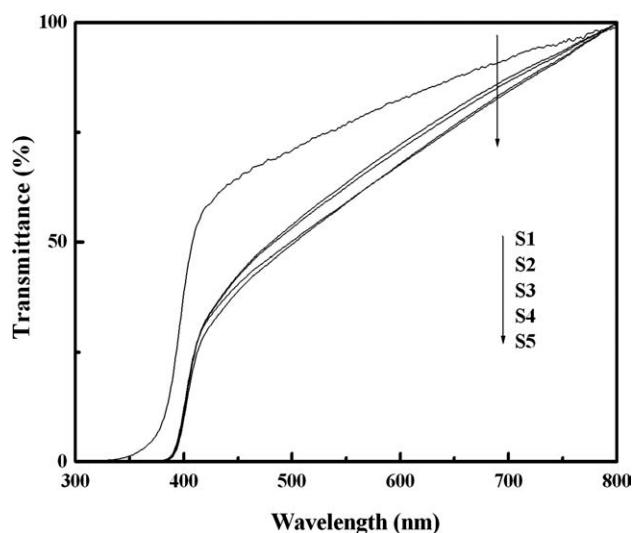


Figure 4 UV-vis spectra of ZnO/epoxy nanocomposites with different weight fractions.

tance may be caused by the surface roughness without polishing and the thickness of the samples.²⁶ The neat epoxy resin shows good visible light transmittance and poor UV-light shielding properties at 300–400 nm. Hence, if the S1 was used as UV-LED encapsulating material, it would induce severe UV-light leaking. Herein, this situation has been significantly improved by appropriately increasing ZnO content. However, while increasing ZnO content, the transmittance shown slightly reduction and UV-light shielding property possessed unobvious difference. The ZnO/epoxy nanocomposite containing only 0.06 wt % ZnO nanoparticles shows very high UV-light shielding property (shielding efficiency $>99.9\%$ at 372 nm) with significantly improvement (63 nm), and indicates a high transmittance of about 87% at 700 nm with only a slight reduction (4%) compared with that of neat transparent epoxy matrix as shown in Figure 4. However, the transmittance of S4 and S5 possess a somewhat lower visible light transmittance at the wavelength 700 nm, which is mainly induced by scattering of agglomerated nanoparticles.^{3,26,27} The transparency of ZnO/epoxy

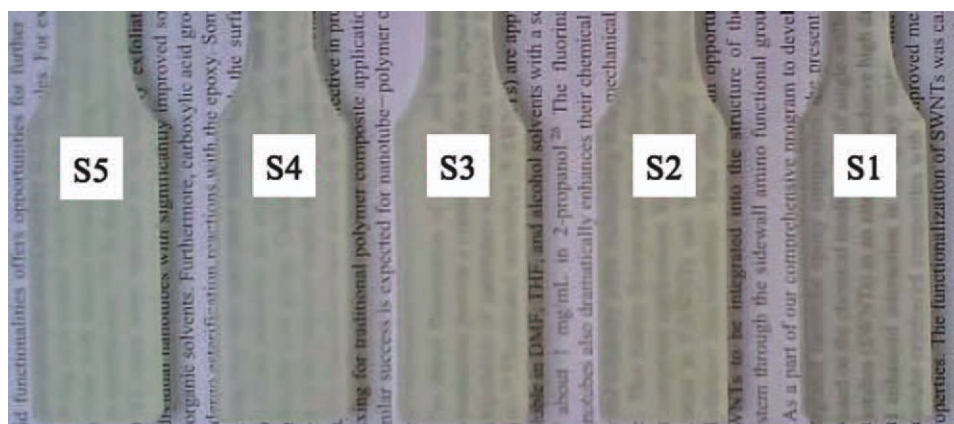


Figure 5 Photographic images of samples S1–S5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nanocomposites with different contents was shown in Figure 5, which agrees well with the visual observation shown in Figure 4.

The reason of successful preparation of ZnO/epoxy composites by above-mentioned procedure is simple to understand. When zinc acetate aqueous solution is added into epoxy resin with vigorous agitation at 30°C (the viscosity of YN1828 is about 6000 mPa s), emulsion is quickly and easily formed due to the epoxy resin YN1828 was insoluble in water. In our experiment, we load of Zn^{2+} cation in water micro-emulsion droplet. When NaOH solution is slowly added into the above emulsion, the OH^- anion was able to react with Zn^{2+} cation quickly in water droplet at the interface of epoxy resin. The high viscosity of epoxy resin plays an essential role in the $\text{Zn}(\text{OH})_2$ particles *in situ* forming, and keeps the particles for dispersion and separation. Whereafter, ZnO/epoxy composites were facilely obtained by the directly thermal treatment of $\text{Zn}(\text{OH})_2$ /epoxy hybrid at 145–150°C for 2 h in a vacuum system under the pressure of -0.1 MPa. The relational reaction is described as follows:

1. $\text{Zn}(\text{Ac})_2 + 2\text{NaOH} = \text{Zn}(\text{OH})_2 + 2\text{NaAc}$
2. $\text{Zn}(\text{OH})_2 = \text{ZnO} + \text{H}_2\text{O}$

CONCLUSIONS

The results showed that the nanocomposite containing an extremely low content (0.06 wt %) of ZnO nanoparticles (around 10–20 nm) had the optimal optical properties, namely high-visible light transparency and high-UV light shielding efficiency, which were the required qualities for transparent packaging materials for LEDs. The ZnO/epoxy nanocomposites were also an excellent candidate for a range of engineering applications, such as parts for

precision optical devices or windows for transportation vehicles etc. In addition, the processability of the packaging material would not change with this very low-ZnO content (0.06 wt %). This preparation technology suggests a simple and controllable route to synthesize metal oxide/polymer nanocomposites in different applied regions.

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