

# Preparation of Phosphor Coated with a Polymer by Emulsion Polymerization and Its Application in Low-Density Polyethylene

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**ABSTRACT:** The long-afterglow phosphor  $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$  is liable to hydrolyze in water with deterioration of its luminescent properties. In this study, *in situ* emulsion polymerization was first used to prepare phosphor coated with poly(methyl methacrylate-*co*-butyl acrylate) [P(MMA-*co*-BA)] to improve water resistance. Fourier transform infrared spectra suggested that the polymer attached to the phosphor by chemical bonding. Observation by scanning electron microscopy (SEM) showed that a polymer layer formed on the surface of the phosphor. The resistance to water of the phosphor coated with the polymer layer was much better than that of the uncoated phosphor because the transparent polymer layer could suppress its hydrolysis process. Low-density poly-

ethylene (LDPE) plastics, doped with long-afterglow phosphors, were manufactured with an extrusion technique. Through coating with P(MMA-*co*-BA), the compatibility of phosphor with the LDPE matrix was improved, as determined by SEM. The luminous LDPE plastics blended with the phosphor coated with polymer showed long and strong phosphorescence with little loss of persistence phosphorescence compared to the uncoated phosphor. The LDPE plastics still retained their mechanical properties through doping with 3% (mass fraction) of the phosphors. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3811–3816, 2008

**Key words:** blending; emulsion polymerization; luminescence

## INTRODUCTION

$\text{Eu}^{2+}$  and  $\text{Dy}^{3+}$  codoped alkaline earth aluminates ( $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ ) have been intensively studied with respect to applications for luminescence since their first observation by Matsuzawa et al.<sup>1</sup> in 1996. This type of long-afterglow phosphor is very different from a conventional ZnS phosphor, and the brightness and decay time of its phosphorescence are more than 10 times better.<sup>1</sup> Furthermore, it shows great luminance and long-lasting photoluminescence with no radiation.<sup>2,3</sup> Recently, it has been widely used in many fields, such as traffic signs, emergency signs, advertising, watches, and textile printing.<sup>4</sup>

Despite its appealing properties, the bad water resistance of  $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$  phosphor in water-

containing environments and its poor compatibility within a polymer matrix limit its applications. So, the improvement of the water resistance and dispersion within polymer matrices of  $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$  phosphor is becoming a key issue.

There have been some studies on inorganic material coatings on phosphor to improve the water resistance of the phosphor, including as silicon dioxide<sup>5,6</sup> and alumina.<sup>7,8</sup> Although these methods may have improved the phosphor's water resistance, they did not improve its compatibility with resin or organic compounds. By coating the phosphor with a polymer layer, phosphor can be homogeneously dispersed in matrices. Recently, Lu and Shu<sup>9</sup> reported the production of  $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$  phosphor coated by poly(methyl methacrylate) (PMMA). However, it was prepared by solution polymerization and toluene was used as the disperse medium.

In this article, a new approach for the preparation of phosphor coated with poly(methyl methacrylate-*co*-butyl acrylate) [P(MMA-*co*-BA)] by *in situ* emulsion polymerization is reported. Although this approach was successfully used previously for the preparation of PMMA/titanium dioxide composite particles,<sup>10</sup> PMMA/SiO<sub>2</sub> composite particles,<sup>11</sup> and poly(styrene-*co*-methyl methacrylate)/SiO<sub>2</sub> composite

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nanoparticles,<sup>12</sup> to the best of our knowledge, no work has been published on the preparation of P(MMA-*co*-BA)/SrAl<sub>2</sub>O<sub>4</sub> : Eu<sup>2+</sup>, Dy<sup>3+</sup> composites.

The ability to combine SrAl<sub>2</sub>O<sub>4</sub> : Eu<sup>2+</sup>, Dy<sup>3+</sup> with matrices to produce luminous plastics has stimulated much research interest. Low-density polyethylene (LDPE) is one of the most important resins because of its relatively transparency, facile processability, and environmental stability. In this study, the phosphor coated with polymer was used to blend with LDPE to manufacture luminous plastics.

## EXPERIMENTAL

### Materials

SrAl<sub>2</sub>O<sub>4</sub> : Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor was provided by Sichuan Xinli Industrial Group Co., Ltd. (Chengdu, China) and had average particle size of about 30 μm. As a comparison, SrAl<sub>2</sub>O<sub>4</sub> : Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor coated by organic Si was also provided by the same company. LDPE, provided by Beijing Yanshan Petrochemical Corp. (Beijing, China), was used as a polymer matrix material for the manufactured plastics. The methyl methacrylate (MMA) and butyl acrylate (BA) were obtained from Kelong Chemical Reagents Factory (Chengdu, China) and were further purified by distillation under reduced pressure before use. The surfactant, sodium dodecyl sulfate and the initiator, potassium persulfate, which were purchased from Beijing Chemical Reagents Factory (Beijing, China), were analytical grade and were used without further purification. The chloroform and the paraffin liquid used in this study were available commercially. Distilled water was used throughout the experiments.

Before polymerization, the SrAl<sub>2</sub>O<sub>4</sub> : Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor was first treated by a sol-gel process to coat the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> films on the surface.<sup>13</sup> Then, it was modified with 8% (mass fraction) of the coupling agent 3-methacryloxypropyl trimethoxysilane (KH-570) in ethanol solution and dried at 80°C to remove the solvent.

### Modification of the SrAl<sub>2</sub>O<sub>4</sub> : Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor

Coating of the SrAl<sub>2</sub>O<sub>4</sub> : Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor with P(MMA-*co*-BA)

The SrAl<sub>2</sub>O<sub>4</sub> : Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor coated by P(MMA-*co*-BA) was prepared by the grafting emulsion polymerization of MMA and BA onto the surface of the phosphor according to the following procedure. First, approximately 1.08 g of sodium dodecyl sulfate was dispersed in 20 mL of distilled water in a round-bottom flask for 20 min at room temperature. Then, about 4.0 g of the phosphor was dispersed into the suspension and stirred for 20 min before the solution was heated to 75°C in a water

bath, and the solution was purged with nitrogen to remove any oxygen, which could have intercepted radicals and disrupted the polymerization. At this point, 0.18 g of potassium persulfate dissolved in 16 mL of distilled water was added to initiate the polymerization. Purified MMA (6.0 g) and BA (2.0 g) monomers were added dropwise to the mixture. Then, the emulsion polymerization was carried out for about 4 h under nitrogen at 75°C before the solution was allowed to cool to room temperature. The obtained products were filtered and washed to remove any unreacted monomer and residual surfactant. The products were subsequently dried, crushed, and stored in a desiccator before use.

### Preparation of the luminous LDPE plastics

The sample was prepared by the blending of LDPE with 3% (mass fraction) of the phosphors and a small amount of paraffin liquid. Experiments were carried out in a twin-screw extruder (Haake Fisons, Rheocord 90) [Madison, Wisconsin, USA]. For the blending experiments, the materials were dry-blended before they were fed into the extruder through a hopper. The screw speed was set at 20 rpm, and the four heating zones of the extruder were set at 170, 185, 185, and 185°C. The extruded strands coming out of the extruder, about 3.2 mm in diameter, were cooled and pelletized with a Brabender Kulturstrasse model 51-55 D-47055 (Duisburg, Germany) and collected for later use. The pelletized batches of approximately 300 g each were fed into an injection-molding machine (Ferromatik Milacron, K-Tec 40, Malterdin, Germany). The injection time and cooling time were both set at 10 s, and the four heating zones of the injection-molding machine were set at 185, 180, 170, and 50°C. After the injection-molding process, the luminous plastics were obtained.

### Characterization

Fourier transformed infrared (FTIR) spectra of the phosphors were recorded on a Nicolet 560 spectrometer [Madison, Wisconsin, USA] with the KBr pellet technique. Before FTIR measurement, all of the phosphors were extracted with chloroform for 10 days in a Soxhlet extractor and dried at 60°C to remove the solvent.

The morphology of dried phosphors and luminous plastics were investigated with a scanning electron microscope (Jeol JSM-5900LV, Tokyo, Japan) operating at 20 kV. The dried samples were coated with gold *in vacuo* before they were viewed by scanning electron microscopy (SEM).

The water resistance properties of the phosphors were measured on a precision pH meter (model LIDA PHS-3C, Shanghai LIDA Instrument Factory, Shanghai, China). This was carried out for the sus-

**TABLE I**  
Chemical Structures of KH-570, MMA, and BA

Chemical agent	Chemical structure
KH-570	$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
MMA	$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3$
BA	$\text{H}_2\text{C}=\text{CHCO}_2(\text{CH}_2)_3\text{CH}_3$

pension, which contained 1.0 g of phosphor and 20.0 g of distilled water under magnetic stirring at room temperature.

Excitation and emission spectra were performed with a Hitachi F-850 spectrofluorometer (Tokyo, Japan). Luminescence decay curves were obtained from a PR-305 fluorescence spectrophotometer (Zhejiang University Sensing Instruments Co. LTD, Hangzhou, China) with a 1040 Lx laser as the excitation source. Before the measurement, the samples were pre-excited for 20 min.

Tensile strength and elongation at break of the plastics were measured on an Instron model 4302 (Instron Co., Canton, Ohio, USA) universal testing instrument, according to the regulation mentioned in National Standard of China GB 1040-1992. Test samples for the tensile strength and elongation measurements (five samples per treatment) were prepared with specimen dimensions of  $50 \times 10 \times 4.3 \text{ mm}^3$ . The initial grip distance was 5.0 cm, and the test speed was set at 50 mm/min. Peak loads and elongation at break of the plastics were recorded.

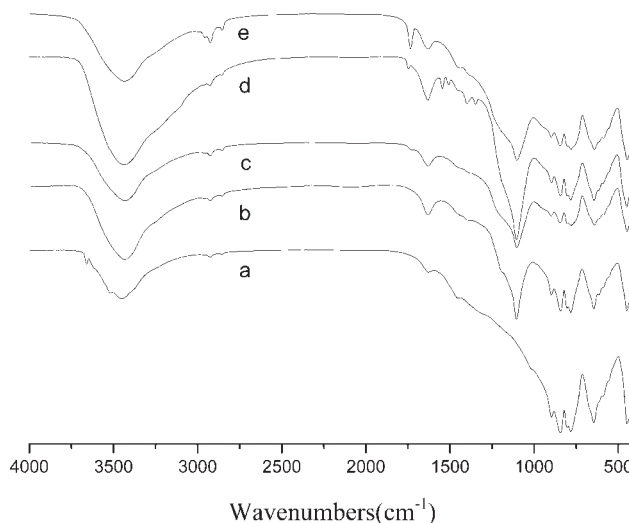
## RESULTS AND DISCUSSION

### Analysis of the chemical structure of the phosphors by infrared spectroscopy

The coupling agent KH-570 had silanol groups, which had strong interactions with hydroxyl groups on the surface of the phosphor coated by  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  films, and vinyl groups, which could react with MMA or BA during the emulsion polymerization. The chemical structures of KH-570, MMA, and BA are shown in Table I.

So, we inferred that the polymer attached to the phosphor by a covalent bond through the coupling agent. To confirm this assumption, phosphor coated with P(MMA-co-BA) and phosphor coated with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  after modification by KH-570 were measured by FTIR spectroscopy. The FTIR spectra of the polymer-coated phosphors are shown in Figure 1. FTIR studies were also carried out on uncoated  $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$  phosphor and phosphor coated by  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  films.

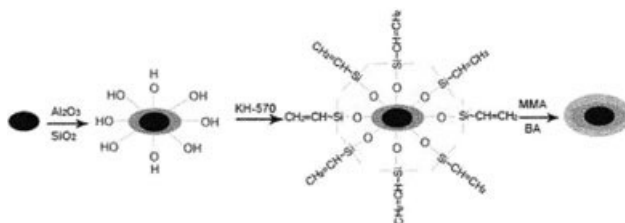
From the spectrum of uncoated  $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$  phosphor, two major peaks at about 3435 and  $1634 \text{ cm}^{-1}$  were observed, which were assigned to the O—H stretching bands and the stretching mode of  $\text{H}_2\text{O}$ , respectively. The absorption bands below



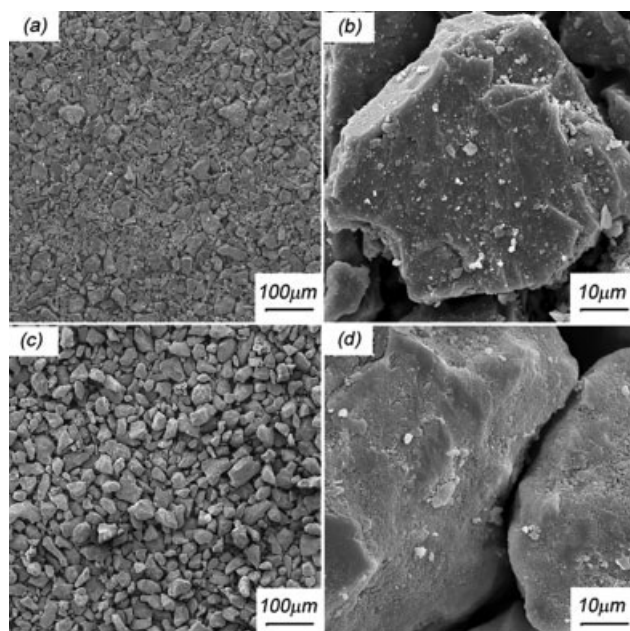
**Figure 1** FTIR spectra of (a) uncoated phosphor, (b) phosphor coated with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , (c) phosphor coated with P(MMA-co-BA) without treatment by KH-570, (d) phosphor coated with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  after modification by KH-570, and (e) phosphor coated with P(MMA-co-BA) after treatment by KH-570.

$1000 \text{ cm}^{-1}$  were attributed to the stretching vibration mode of the  $\text{SrAl}_2\text{O}_4$  structure. Compared to the uncoated  $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$  phosphor, all of the coated phosphors had new peaks at about  $1100 \text{ cm}^{-1}$  corresponding to the asymmetric stretching mode of Si—O—Si due to  $\text{SiO}_2$  coated on the phosphor. Furthermore, a small decrease in the intensity of the peaks below  $1000 \text{ cm}^{-1}$  was observed.

Comparing the spectrum of phosphors coated with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  after modification by KH-570, we observed a significant increase in the intensity of the peak at  $1735 \text{ cm}^{-1}$  corresponding to the carbonyl ( $=\text{C}=\text{O}$ ) stretching bands of the phosphor coated with P(MMA-co-BA), due to the adhesion of the polymer to the phosphor. The spectrum of the phosphor coated with P(MMA-co-BA) without treatment by KH-570 and the phosphor only coated with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were almost the same. This indicated that after extraction with chloroform for 10 days, the polymer physically adsorbed on the surface of the phosphor was completely eliminated. So, we concluded that after treatment by KH-570, the polymer



**Scheme 1** Formation process of  $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$  phosphor coated by P(MMA-co-BA).



**Figure 2** SEM images of (a,b) uncoated phosphor and (c,d) phosphor coated with P(MMA-co-BA) after treatment by KH-570. Amplification: (a) 100, (b) 1500, (c) 100, and (d) 1500 $\times$ .

coating on the phosphor involved a chemical bonding process during the emulsion polymerization. The possible process is shown in Scheme 1.

#### Morphology of the $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor coated with P(MMA-co-BA)

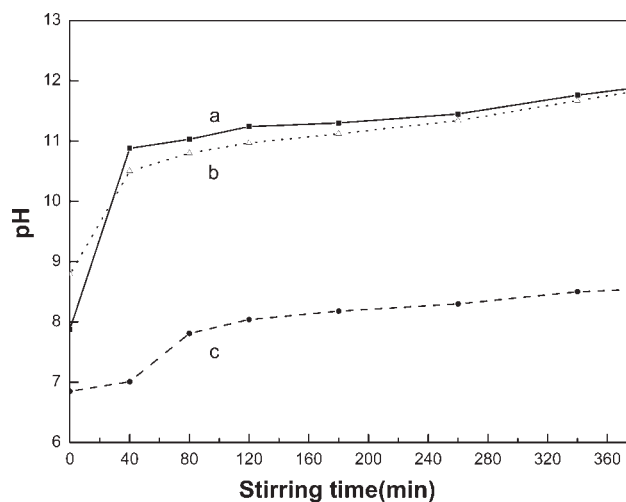
The differences in the appearance and uniformity of the uncoated phosphor and the phosphor coated with P(MMA-co-BA) can be compared with the SEM images shown in Figure 2. As shown in Figure 2, it is clear that the phosphors contained irregular particles with a wide size distribution, and after coating with P(MMA-co-BA), the phosphor particles were not so aggregated. In addition, these pictures clearly show the smooth surfaces of the uncoated phosphor compared to the rough surfaces of the phosphor coated with P(MMA-co-BA). The homogeneous white layer of the composite particles was probably due to the polymerization of MMA and BA on the surface of the phosphor.

#### Water resistance of the phosphors

It is well known that the  $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$  phosphor hydrolyzes dramatically when immersed in water; the process of this hydrolyzation is illustrated in Scheme 2.



**Scheme 2** Schematic diagram of the hydrolyzation process of  $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ .



**Figure 3** pH value versus time for different phosphor solutions under stirring: (a) uncoated phosphor, (b) phosphor coated with organic Si, and (c) phosphor coated with P(MMA-co-BA).

The pH value variation for different phosphors under stirring in water at room temperature for 6 h is shown in Figure 3. Obviously, the uncoated phosphor and phosphor coated with organic Si hydrolyzed dramatically in the 1st hour when the pH values of their aqueous suspensions changed from 8 to about 11. After 6 h, they hydrolyzed almost completely, and the product was a kind of white particle that gave no light emission. In contrast, the pH value of the aqueous suspension of the phosphor coated with P(MMA-co-BA) was maintained at 8 after it was stirred in water for 6 h. This indicated that the P(MMA-co-BA) coated on the surface of the phosphor restrained the procedure of hydrolysis and improved the water resistance of the phosphor.

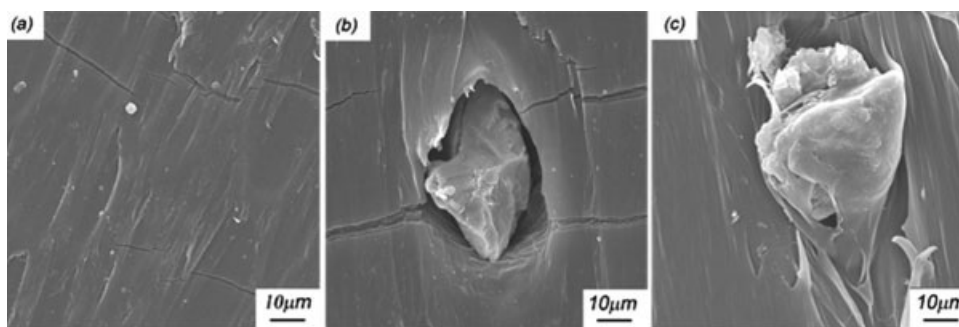
#### Morphology of the luminous LDPE plastics

As shown in Figure 4, the surface of the uncoated phosphor was smooth compared to the rough surface of the phosphor coated with P(MMA-co-BA), which is consistent with the results from Figure 2, and the interface between the phosphor and LDPE substrate was very clear. The acute edge of the uncoated phosphor is disadvantageous for use.

The phosphor coated with P(MMA-co-BA) adhered well to the LDPE matrix and showed an unclear interface between the phosphor and LDPE matrix, which indicated that coating P(MMA-co-BA) on the surface of the phosphor could improve its compatibility with resin or organic compounds. Then, the mechanical properties of the luminous plastics could be improved.

#### Photoluminescence properties of the luminous LDPE plastics

The excitation and emission spectra of the luminous LDPE plastics are shown in Figure 5. The results



**Figure 4** SEM images of the LDPE plastics (a) without phosphor, (b) blended with uncoated phosphor, and (c) blended with phosphor coated with P(MMA-co-BA).

indicate that there were no obvious changes for the excitation and emission spectra, excluding a small decrease in the photoluminescence intensity. All of the phosphor samples exhibited three major excitation peaks at 260 and 440 nm in addition to the maximum at 360 nm on the excitation spectrum. They all exhibited broad band emission spectra, which peaked at 520 nm and were attributed to the  $4f^{65d}-4f^7$  transition of  $\text{Eu}^{2+}$ .<sup>14,15</sup> This revealed that the crystal structure of the phosphors was not destroyed during the coating process. The luminescence intensity of the phosphor coated with P(MMA-co-BA) was a little weaker than that of uncoated phosphor. This was probably because of the additional layer of polymer coating on the surface of the phosphor, which reflected the exciting light and reduced the excitation energy absorbed by the phosphor.

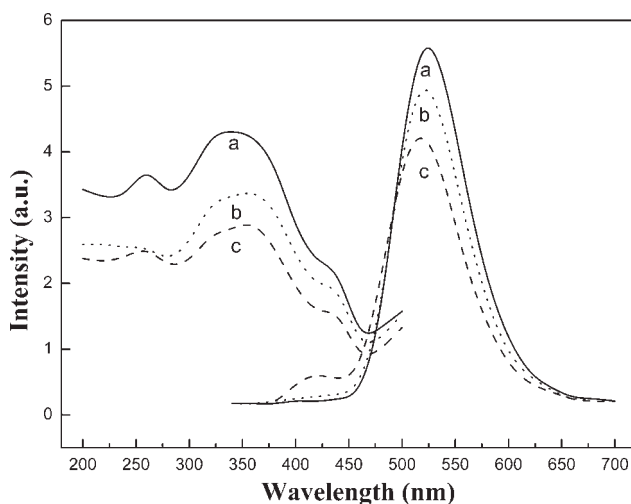
The luminescence decay curves of the luminous LDPE plastics are illustrated in Figure 6. Both the luminous plastics blended with uncoated phosphor and the phosphor coated with P(MMA-co-BA)

showed similar afterglow characterizations; their spectra coincided exactly. Their initial luminescence intensity was much higher than that of the luminous plastics blended with phosphor coated with organic Si.

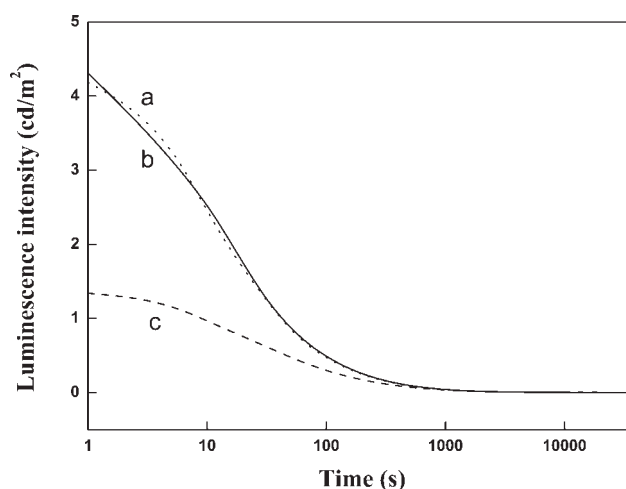
In industry, the *phosphorescence decay time* is defined as the duration from the moment of stopping the light excitation to the moment when the emission light intensity is reduced to  $0.32 \text{ mcd/m}^2$  (i.e., 100 times the perception limit of the human eye).<sup>16</sup> The phosphor coated with P(MMA-co-BA) maintained its phosphorescence intensity above this level well for over 8 h, just as the uncoated phosphor did.

### Mechanical properties of the LDPE plastics

As shown in Table II, the tensile strengths of neat LDPE and LDPE blended with phosphors were almost consistent. So, we inferred that the phosphors had no significant impact on the LDPE matrix. It is



**Figure 5** Photoluminescent spectra of the luminous LDPE plastics blended with (a) uncoated phosphor, (b) phosphor coated with P(MMA-co-BA), and (c) phosphor coated with organic Si.



**Figure 6** Luminescence decay curves of the luminous plastics blended with (a) uncoated phosphor, (b) phosphor coated with P(MMA-co-BA), and (c) phosphor coated with organic Si.

**TABLE II**  
**Mechanical Properties of LDPE and LDPE Blended with Phosphors**

Sample	Tensile strength (MPa)	Elongation at break (%)
LDPE	12.39	93
LDPE (uncoated phosphor)	12.12	85
LDPE (phosphor coated with organic Si)	12.19	79
LDPE [phosphor coated with P(MMA- <i>co</i> -BA)]	12.12	89

well known that the incorporation of filler particles usually decreases the elongation of filled polymer composites because of the intrinsic stiffness of the inorganic filler. When the phosphors were treated in the presence of the coupling agent and coated with P(MMA-*co*-BA), the surface of the luminous particles was modified, which may have led to an improvement in the mechanical properties of the luminous LDPE plastics. So, compared to the uncoated phosphor, the luminous LDPE plastics blended with phosphor coated with P(MMA-*co*-BA) had higher elongations.

### CONCLUSIONS

In summary, *in situ* emulsion polymerization allowed polymer coating on the surface of phosphors with covalent bonding after they were treated by a coupling agent. By comparison with the

uncoated phosphor, the phosphor coated with P(MMA-*co*-BA) showed better water resistance and good compatibility with LDPE and maintained its photoluminescence properties. The coating ended the resin with luminescence properties and did not affect their mechanical properties too much. Such characteristics should provide new potential applications in a number of technological fields, such as luminous coating, luminous plastics, and other products.

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