

# Preparation of Poly(butyl acrylate)-Poly(methyl methacrylate) (Core-Shell)/Phosphor Composite Particles and its Application in PVC Matrix

Tonghua Chen,<sup>1</sup> Peng Xu,<sup>1</sup> Yongyue Luo,<sup>1</sup> Long Jiang,<sup>1</sup> Yi Dan,<sup>1</sup> Li Zhang,<sup>2</sup> Kun Zhao<sup>2</sup>

<sup>1</sup>State Key Laboratory of Polymer Materials Engineering of China, Polymer Research Institute of Sichuan University, Chengdu 610065, China

<sup>2</sup>Sichuan Xinli Industrial Group Company, Limited, Chengdu 610031, China

Received 11 December 2008; accepted 23 March 2009

DOI 10.1002/app.30472

Published online 8 June 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Luminescent poly(vinyl chloride) (PVC) plastics filling with long afterglow phosphor (SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup>) were prepared via melt blending. To improve the dispersion degree of the phosphor particles and endow the compatibility with PVC matrix, SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> was first grafted with poly(butyl acrylate)-poly(methyl methacrylate) (core-shell) (designed as PMMA(PBA)) by *in situ* emulsion polymerization. The properties of polymer/phosphor composite particles were characterized by fourier transform infrared, X-ray photoelectron spectroscopy, and thermogravimetric analysis. The results show that the polymer had grafted onto the phosphor by chemical bond and the grafting ratio was about 6.3%. The results for PVC

plastics characterized by scanning electron microscopy show that the interfacial adhesion was enhanced with filling the polymer/phosphor composite particles and the compatibility of phosphor with PVC matrix was improved by coating with PMMA(PBA). And the luminescent PVC plastics filled with PMMA(PBA)/phosphor composite particles show improved mechanical properties and higher phosphorescence when the filling content was more than 3 phr compared with the unmodified phosphor. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 496–502, 2009

**Key words:** core-shell polymers; emulsion polymerization; luminescence; poly(vinyl chloride)

## INTRODUCTION

The phosphors based on alkaline earth aluminates activated by Eu<sup>2+</sup> have attracted many attentions since they were first reported by Palilla in 1968.<sup>1</sup> In the recent years, Eu<sup>2+</sup> and Dy<sup>3+</sup> co-doped alkaline earth aluminates (SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup>) have been proved to be one of the most efficient host materials for long-lasting phosphorescence since their first observation by Matsuzawa in 1996.<sup>2</sup> The brightness and decay time of this long afterglow phosphor are almost 10 times more than those of the conventional ZnS : Cu phosphor.<sup>2</sup> The properties of high brightness, nonradioactive, long-lasting photoluminescence, good chemical stability, and excellent environmental capability all result in its wide applications in many fields, such as traffic signs, emergency signs, advertising and interior decoration, and in textile printing.<sup>3–5</sup>

As for the practical application, luminescent plastics filled with phosphor (SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup>) such as poly(methyl methacrylate) (PMMA),<sup>6,7</sup> polysty-

rene (PS),<sup>8</sup> polypropylene<sup>9,10</sup> have stimulated much research interest. As we know, poly(vinyl chloride) (PVC) is an important commodity thermoplastic resin that is extensively used in many construction applications, such as underground pipes, doors, windows, and outdoor building materials, owing to its high mechanical strength, high corrosion resistance, and relatively low cost. Though various nanofillers, including calcium carbonate,<sup>11–13</sup> silica,<sup>14,15</sup> and montmorillonite,<sup>16–18</sup> were reported to prepare PVC composites. In this work, SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor was used to prepare luminescent PVC plastics for the first time, while the phosphor must be modified to improve the mechanical properties of the filled polymer composites. For example, stearic acid,<sup>19</sup> silane coupling agents,<sup>20</sup> and dimethyl silicone have been applied to modify the surface of the phosphor. As acrylate polymers have solubility parameters very close to that of PVC, PMMA(PBA)/phosphor composite particles prepared by *in situ* emulsion polymerization was reported in this article. Although this approach has previously been successfully used for preparation of poly(methyl methacrylate)/titanium dioxide composite particles,<sup>21</sup> PMMA/SiO<sub>2</sub> composite particles,<sup>22</sup> poly(styrene-co-

Correspondence to: Y. Dan (danyichenweiwei@163.com).

methyl methacrylate)/SiO<sub>2</sub> composite particles,<sup>23</sup> poly(methyl methacrylate)/nano-ZnO composite particles,<sup>24</sup> and PS/alumina composite nanoparticles,<sup>25</sup> to our knowledge, no work has been published on the preparation of PMMA(PBA)/SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> composites. Then the phosphor composite particles were employed to fill with PVC to manufacture luminescent plastics. The effects of filling content on performance of PVC plastics were investigated. The results exhibit that PVC plastics filled with PMMA(PBA)/phosphor composite particles have superior mechanical performance, enhanced interfacial adhesion and improved photoluminescence properties than that of unmodified phosphor.

## EXPERIMENTAL

### Materials

SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor was supplied by Sichuan Xinli Industrial Group Co., (Chengdu, China), with average particle size of about 30 μm. Polyvinyl chloride (PVC) used was SG-5 (provided by Yibin Tianyuan Group Co., Yibin, China). The coupling agent, 3-methacryloxypropyl-trimethoxysilane (MPTMS), was from Ha'erbin Chemical Research Institute (Ha'erbin, China). Methyl methacrylate (MMA) and butyl acrylate (BA) were obtained from Kelong Chemical Reagents Factory (Chengdu, China) and were further purified by distillation under a reduced pressure before use. Divinylbenzene (DVB) was used as received. The surfactant, sodium dodecyl sulfate (SDS) and the initiator, potassium persulfate (KPS), which were purchased from Beijing Chemical Reagents Factory (Beijing, China), were of analytical grade and used without further purification. Heat stabilizer, polyethylene (PE) wax, and stearic acid were industrial grade products commercially available. Deionized water was used throughout the experiment.

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

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 SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> films on the surface.<sup>26</sup> Then it was modified by coupling agent 3-methacryloxypropyl-trimethoxysilane (MPTMS). A typical process was as follows: 60 g of phosphor particles and 240 g of 95% ethanol were placed into a flask equipped with a mechanical stirrer. MPTMS (8 wt % to phosphor) was added under rapid stirring. The mixture was heated and reacted for 6 h at 75°C. Afterward, the phosphor was filtrated and extracted with ethanol to remove the excess MPTMS absorbed on the particles. The product was finally dried at 80°C under vacuum condition for 24 h.

### Preparation of the PMMA(PBA)/SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor composite particles

A typical preparation process was described as follows: deionized water (450 mL) and SDS (16.2 g) were first charged into a 1000 mL round-bottom flask equipped with a mechanical stirrer, a dropping funnel, and a nitrogen gas inlet. Then 60 g pre-treated phosphors were dispersed into the SDS aqueous solution and stirred for 20 min, and the solution was purged with nitrogen to remove any oxygen. The reaction mixture was heated to 75°C, and 90 mL of 3% of KPS aqueous solution was added to initiate the polymerization. After that a mixture of about 30 g BA and 0.6 g DVB monomers was added slowly into the mixture, and the emulsion polymerization was carried out for about 2 h under nitrogen at 75°C. At this point, 90 g purified MMA was added dropwise and the reaction was continued for about 3 h before allowed to cool to room temperature. The products obtained were filtered, washed and subsequently dried, and crushed. After that the PMMA(PBA)/phosphor composite particles were obtained. And before the measurements, the phosphor composite particles were extracted with chloroform (CHCl<sub>3</sub>) at 70°C for 10 days in a Soxhlet extractor to remove the ungrafted polymer completely, and dried at 80°C to remove the solvent.

### Preparation of luminescent PVC plastics filled with phosphors

The luminescent PVC plastics were formulated with 100 phr PVC resin, 4 phr heat stabilizer, 0.5 phr stearic acid, and 0.3 phr external lubricant polyethylene (PE) wax, as well as various content of phosphors particles (3, 6, 9, 12 phr). The formulations were initially dry mixed in a high-speed mixer (Model MJ 0.75/1.1, Chongqing, China) for 5 min. And then the mixture was melt mixed with a two-roll mixer (Model SK-16B, Shanghai, China) at 170-175 °C for 10 min. The resulting sheet was compression molded into sheets of 1 mm and 4 mm in thickness by hot pressing at 180°C and 10 MPa for 10 min, using a vulcanization machine (Model HP-63(D), Shanghai, China), followed by cooling to room temperature at 10 MPa. The sheets were prepared for structure characterization and physical properties measurements.

## CHARACTERIZATION

### FTIR measurement

Fourier transformed infrared (FTIR) spectra of the samples were recorded on a Nicolet 560 spectrometer with the KBr pellet technique.

### XPS measurement

The elemental composition of the phosphors was studied using X-ray photoelectron spectroscopy (XPS) on a Kratos XSAM 800 spectrometer (Manchester, Britain), with an Al monochromatic X-ray source (1486.6 eV).

### TGA measurement

The thermal degradation characteristics of the phosphors were performed on a universal V4.4A TA instruments (SDT Q600) under a flowing nitrogen atmosphere (100 mL/min). The heating rate was 10°C/min and the scanning temperature was in the range from room temperature to 600°C.

### Mechanical properties measurement

Tensile strength tests were carried out with an Instron Model 5567 (Canton, MA) universal testing instrument, with a crosshead speed of 20 mm/min and a cell load of 1 kN. Charpy notched impact samples with dimensions  $65 \times 10.5 \times 4 \text{ mm}^3$  were tested by a Model ZBC-4B (Shenzhen, China) impact testing machine according to the regulation mentioned in GB/T 1043-93. All mechanical tests were conducted at ambient temperature (20–25°C) and the average value of five repeated tests was taken for each sample.

### Scanning electron microscopy

The morphologies of the fracture surfaces of the PVC plastics were observed in a scanning electron microscope (SEM: JEOL JSM-5900LV, Japan) operating at 20 kV. The SEM samples were prepared in liquid nitrogen for 30 min, and then broken into two pieces. The fractured surfaces of specimens were coated with a thin layer of gold before SEM examination.

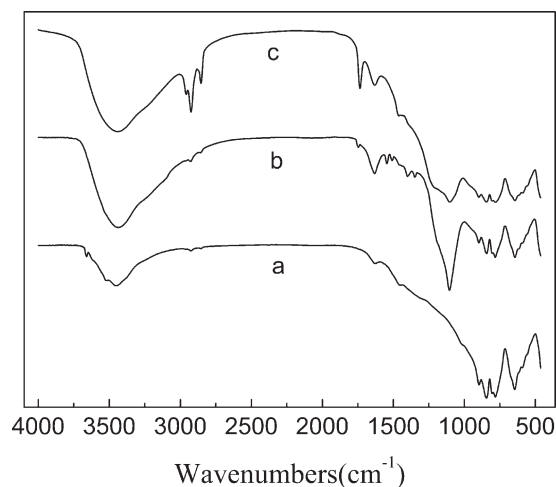
### Photoluminescence characterization

Photoluminescent excitation and emission spectra of the luminescent PVC plastics (the thickness of the PVC plastics is 1 mm) were recorded using a Hitachi F-850 spectrofluorimeter.

## RESULTS AND DISCUSSION

### FTIR spectra of the phosphors

Figure 1 shows the FTIR spectra of unmodified  $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$  phosphor, MPTMS/phosphor composite particles, and extracted PMMA(PBA)/phosphor composite particles. From the spectrum of unmodified  $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$  phosphor [Fig.

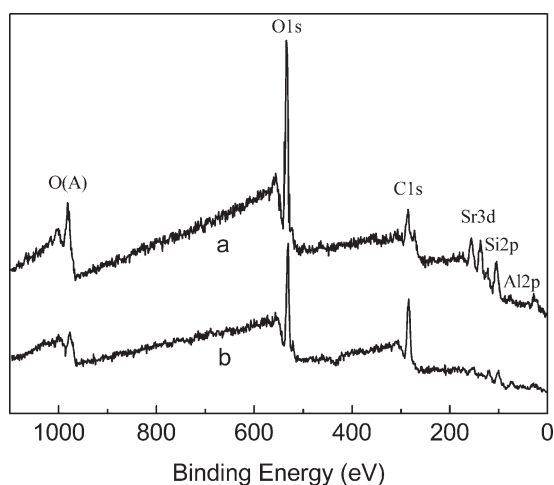


**Figure 1** FTIR spectra of (a) unmodified phosphor, (b) MPTMS/phosphor composite particles, and (c) PMMA(PBA)/phosphor composite particles.

1(a)], two major absorption band at about  $3435 \text{ cm}^{-1}$  and  $1634 \text{ cm}^{-1}$  which can be assigned to the O—H stretching bands and the stretching mode of  $\text{H}_2\text{O}$ , respectively, are observed. The absorption bands below  $1000 \text{ cm}^{-1}$  can be attributed to the stretching vibration mode of the  $\text{SrAl}_2\text{O}_4$  structure. Compared with the spectrum of unmodified phosphor, there are new absorption appeared in the spectra of MPTMS/phosphor composite particles [Fig. 1(b)] and extracted PMMA(PBA)/phosphor composite particles [Fig. 1(c)] at about  $1100 \text{ cm}^{-1}$  corresponding to the asymmetric stretching mode of Si—O—Si because of  $\text{SiO}_2$  coated on the phosphor. Compared with MPTMS/phosphor composite particles, the intensity of the absorption band at  $1735 \text{ cm}^{-1}$  which is attributed to the carbonyl ( $>\text{C}=\text{O}$ ) stretching bands, and the absorption at  $2925 \text{ cm}^{-1}$  and  $2854 \text{ cm}^{-1}$ , which are assigned to the asymmetric and symmetric stretching of methylene ( $>\text{CH}_2$ ), respectively, for PMMA(PBA)/phosphor composite are more pronounced, which is due to the adhesion of the polymer onto the phosphor. While after extracted with chloroform for 10 days, the polymer physically absorbed on the surface of the phosphor can be completely eliminated. So it can be concluded that polymer coated on phosphor involves chemical bonding process during emulsion polymerization.

### X-ray photoelectron spectroscopy (XPS) studies of the phosphors

To study the elemental composition of the phosphors, XPS studies were undertaken. The XPS spectra of the unmodified  $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$  phosphor and the PMMA(PBA)/phosphor composite particles (Fig. 2) exhibit three major peaks at 532, 285, and 104 eV, corresponding to O1s, C1s, and Si2p



**Figure 2** XPS spectra of (a) unmodified phosphor and (b) PMMA(PBA)/phosphor composite particles.

photoemission. Two minor peaks at about 136 and 75 eV which can be assigned to Sr3d and Al2p photoemission are also detected. And it can be observed that the C1s signal of the phosphor increases after the modification of polymer coating.

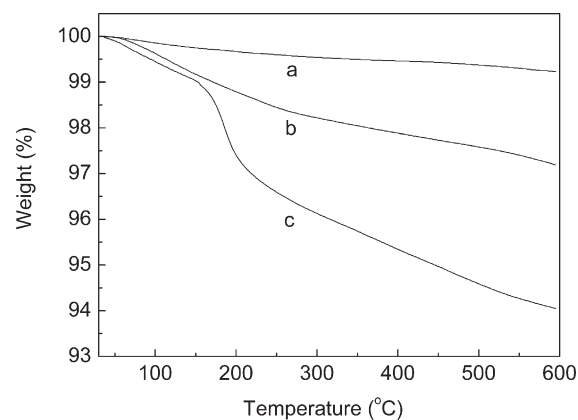
The elemental composition of the SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor and the phosphor composite particles are summarized in Table I. As shown in the Table, it is clear that the element content of carbon in the phosphor composite particles is much higher at 55.3%, compared with the SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor at only 27.8%. So it can be concluded that the polymer were coated on the surface of the phosphor.

**Thermogravimetry analysis (TGA) of the phosphors**

Figure 3 shows the thermogravimetry analysis (TGA) plots of unmodified phosphor, MPTMS/phosphor composite particles, and extracted PMMA(PBA)/SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor composite particles. From this figure, it is clear that the original phosphor does not decompose below 600°C [Fig. 3(a)], and the weight loss about 0.8% is prob-

**TABLE I**  
Element Composition of the SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> Phosphor and the Phosphor Composite Particles

Element	Content (%)	
	The SrAl <sub>2</sub> O <sub>4</sub> : Eu <sup>2+</sup> , Dy <sup>3+</sup> phosphor	The phosphor composite particles
C1s	27.8	55.3
O1s	49.7	34.9
Si2p	13.2	5.6
Sr3d	3.6	0.3
Al2p	5.7	3.9

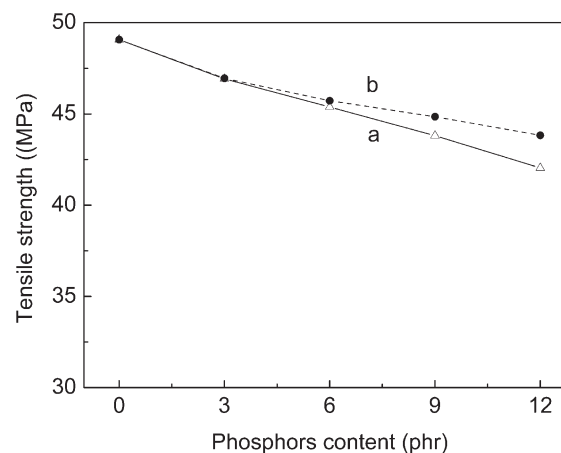


**Figure 3** TGA curves of (a) unmodified phosphor, (b) MPTMS/phosphor composite particles, and (c) PMMA(PBA)/phosphor composite particles.

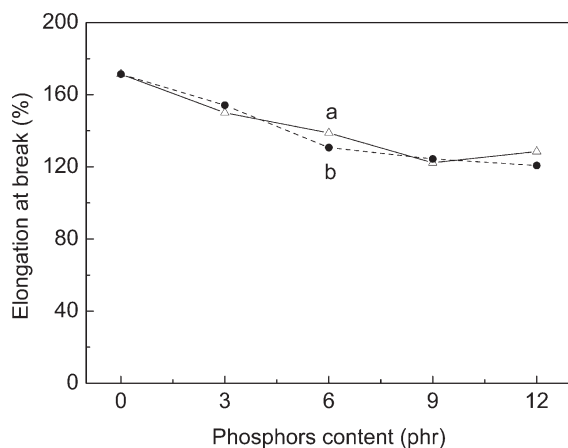
ably because of the removal of absorbed water. The weight loss of MPTMS/phosphor composite particles is about 2.8% [Fig. 3(b)] and it can be considered to the existence of crystal water and grafting MPTMS. As the PMMA(PBA)/SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor composite particles were Soxhlet extracted with CHCl<sub>3</sub> at 70°C and constant pressure for 10 days to remove the physically absorbed polymer completely, the weight loss between 150°C and 600°C [Fig. 3(c)] can be attributed to the existence of chemically grafting polymer. So it can be also confirmed that the polymer attached to the phosphor involves chemical bonding. The percentage of the remains is 94.1%, so the grafting percentage is about 6.3%.

**Mechanical properties of PVC plastics**

The tensile strength of neat PVC (phosphors content = 0 phr) and luminescent PVC composites as a function of filling phosphor content is given in Figure 4.



**Figure 4** Effect of phosphor contents on tensile strength of luminescent PVC plastics filled with (a) unmodified phosphor and (b) PMMA(PBA)/phosphor composite particles.



**Figure 5** Effect of phosphor contents on elongation at break of luminescent PVC plastics filled with (a) unmodified phosphor and (b) PMMA(PBA)/phosphor composite particles.

As shown in Figure 4, the tensile strength of luminescent PVC plastics decreases with the content of phosphors added, but the tensile strength of PVC plastics filled with PMMA(PBA)/phosphor composite particles is higher than that of unmodified phosphor when the content of phosphor is higher than 3 phr. It is known that the tensile strength of composites is influenced by the filler fraction and the interfacial adhesion between particles and matrix. With the addition of the phosphor particles, the cross section area of composites to bear load decrease, and only a small amount of stress could be transferred from the matrix to inorganic particles. Also the phosphor particles in PVC matrix would create physical defect in the luminescent plastics. Thus the tensile strength of the luminescent PVC plastics decreases with increasing content of phosphor particles. The PMMA(PBA)/phosphor composite particles should have higher interfacial interaction with PVC matrix because of the compatibility of PMMA with PVC matrix. Consequently, the interface could transfer more stress from PVC matrix to the composite particles, thus the PVC plastics filled with them have enhanced tensile strength in comparison with that of unmodified phosphor.

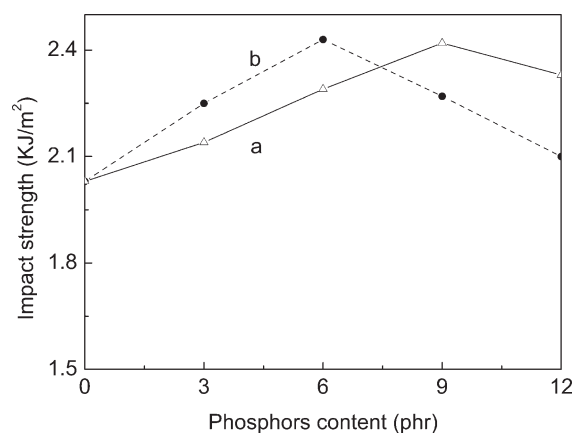
Figure 5 presents the elongation at break of neat PVC and luminescent PVC composites as a function of filling phosphor content. It is well known that incorporation of filler particles usually decreases elongation of filled polymer composite because of the intrinsic stiffness of the inorganic filler. As shown in Figure 5, elongation at break of PVC filled both with unmodified phosphor and PMMA(PBA)/phosphor composite particles decreases slightly with the content of phosphors. It indicates that coating the phosphor with polymer will not affect elongation at break of the PVC plastics.

Figure 6 plots the Charpy notched impact energy of neat PVC and luminescent PVC composites as a function of phosphor content. From this figure, it can be seen that the impact strength of all PVC composites is higher than that of neat PVC. When the phosphor particles are dispersed in the PVC matrix, the particles could act as stress concentration sites which could promote cavitations at the particle-matrix boundaries and lead to the formation of cracks in the matrix. The cavitations could release the plastic constraints and trigger mass plastic deformation of the matrix, and the cracks created in the composite could absorb the impact energy, thus the toughness of composites would be improved.

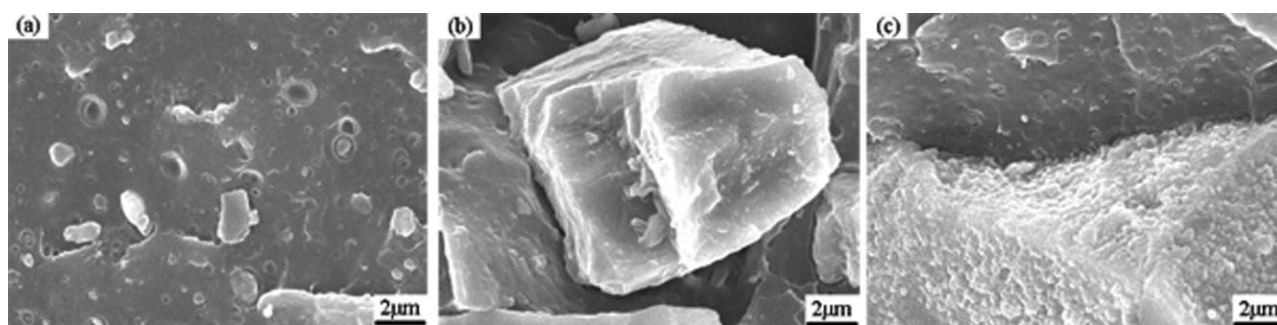
The compatibility of phosphor with PVC would be improved after coated by polymer, as PMMA having a solubility parameter ( $\delta$ ) very close to that of PVC ( $\delta(\text{PVC}) = 9.5\text{--}9.7$ ,  $\delta(\text{PMMA}) = 9.3$ ). So higher interfacial interaction with PVC matrix will be achieved and the impact stress could be easily transferred from PVC matrix to PMMA(PBA)/phosphor composite particles. This will lead to the improvement of the impact toughness of the composites. It is also noted that the impact strength of PVC filled with PMMA(PBA)/phosphor composite particles increases with increasing filling contents until 6 phr, which reaches a maximum ( $2.43 \text{ kJ/m}^2$ ). Further increase in particle loading gives lower impact strength because of the aggregation effect of the phosphors particles in the PVC matrix. The defects to composites caused by the aggregation of the phosphors increase, so the impact strength of the composites would be decreased.

#### Morphology of fractured surface of PVC plastics

Figure 7 shows the SEM micrographs of the fracture surfaces of PVC and luminescent PVC composites



**Figure 6** Effect of phosphor contents on impact strength of luminescent PVC plastics filled with (a) unmodified phosphor and (b) PMMA(PBA)/phosphor composite particles.



**Figure 7** SEM micrographs of fractured surfaces of PVC plastics (a) neat PVC, (b) filled with 3 phr unmodified phosphor, and (c) filled with 3 phr PMMA(PBA)/phosphor composite particles.

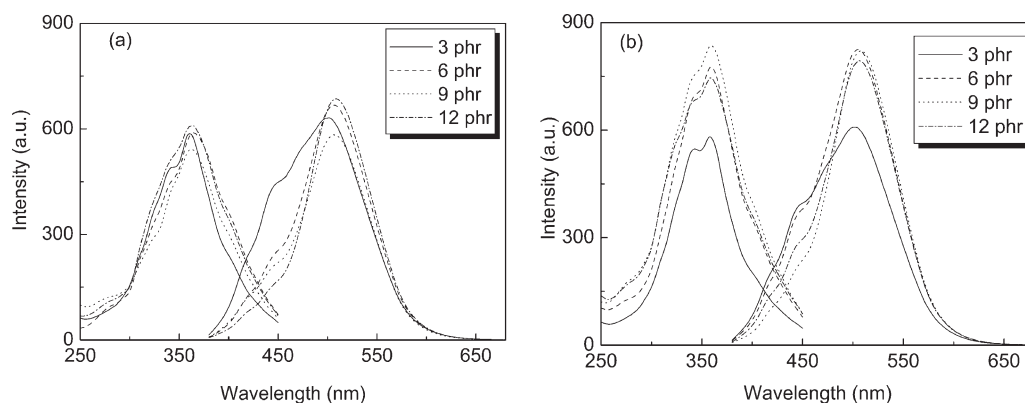
filled with 3 phr phosphor particles. As shown in Figure 7, compared with the unmodified phosphor, the surface of the PMMA(PBA)/phosphor composite particles is rough because of the polymer layer. The weak interaction between unmodified phosphor and PVC matrix can be observed, resulting from the aggregation of unmodified phosphor and poor compatibility between phosphor fillers and PVC matrix. And the interfacial adhesion is improved when filling with PMMA(PBA)/phosphor composite particles. It may be caused by the excellent compatibility of PMMA with PVC. So coating PMMA(PBA) on the surface of the phosphor can improve its compatibility with PVC, and the mechanical properties of the luminescent PVC filled with PMMA(PBA)/phosphor composite particles can be improved.

### Photoluminescence properties of luminescent PVC plastics

The excitation and emission spectra of the luminescent PVC plastics filled with different content of phosphor particles are shown in Figure 8. We can see from the spectra that all the luminescent PVC plastics samples exhibit excitation spectrum peak-

ing at 360 nm. And all the emission spectra of luminescent PVC plastics show a strong green band at about 510 nm which is attributed to the  $4f^65d-4f^7$  transition of  $\text{Eu}^{2+}$ .<sup>27,28</sup> It reveals that crystal structure of phosphor has not been destroyed after coated with polymer. While the peak luminescence intensity for PVC filled with PMMA(PBA)/phosphor composite particles is a little weaker than that of PVC filled with unmodified phosphor when the content of phosphor is 3 phr. This is probably because of the additional layer of polymer coating on the surface of the phosphor which reflects, absorbs or scatters part of the light and reduces the intensity of emission peak.

The luminescence intensity of PVC filled with PMMA(PBA)/phosphor composite particles is higher than that of PVC filled with unmodified phosphor when the content of phosphor is more than 6 phr. The reason may be caused by the adhesion of Fe to the unmodified phosphor during the blending process because of its high stiffness (the stiffness index of  $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$  is about 7). When the addition of unmodified phosphor increases, the blackening of PVC caused by the metal is so severe that the luminescence intensity does not increase. While the degree of black-



**Figure 8** Effect of phosphor contents on luminescent spectra of luminescent PVC plastics filled with (a) unmodified phosphor and (b) PMMA(PBA)/phosphor composite particles.

ness of PVC filled with PMMA(PBA)/phosphor composite particles can be inhibited because the friction between the phosphor composite particles with the processing equipment will be avoid because of the polymer layer coating on the surface of the phosphor, so that their luminescence intensities can be improved.

### CONCLUSIONS

The PMMA(PBA)/SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor composite particles could be prepared by *in situ* emulsion polymerization of monomers in the presence of SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor. The polymer is chemically grafted onto the phosphor surface and the grating ratio is about 6.3%. Comparing with unmodified phosphor, the PMMA(PBA)/phosphor composite particles show enhanced interfacial adhesion and good compatibility with PVC matrix. By introducing the PMMA(PBA)/SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor composite particles to PVC, the luminescence PVC plastics can be obtained. And the obtained luminescent PVC plastics provide new potential applications in a number of construction fields, such as luminescent doors, windows, and other outdoor building materials.

The authors are grateful to the National Natural Science Foundation of China (No. 20374036) and the Key Project Foundation of Sichuan Province of China (No. 04GG009-010-2) for support of this research

### References

1. Palilla, F. C.; Levine, A. K.; Tamkus, M. R. *J Electrochem Soc* 1968, 115, 642.
2. Matsuzawa, T.; Aoki, Y.; Takeuchi, N.; Murayama, Y. *J Electrochem Soc* 1996, 143, 2670.
3. Groppi, G.; Cristiani, C.; Forzatti, P. *J Mater Sci* 1994, 29, 3441.
4. Yamamoto, H.; Matsuzawa, T. *J Lumin* 1997, 72, 287.
5. Aitasalo, T.; Deren, P.; Holsa, J.; Jungner, H.; Krupa, J. C. *J Solid State Chem* 2003, 171, 114.
6. Shao, K.; Li, H.; Zhang, J.; Liu, X.; Li, M. *Plast Sci Technol* 2005, 4, 20.
7. Pu, H.; Su, F. *China Plast Ind* 1998, 26, 113.
8. Pu, H.; Su, F.; Yuan, Y. *J Build Mater* 1998, 1, 160.
9. Zhang, J.; Shao, K.; Wang, W. *Eng Plast Appl* 2005, 33, 23.
10. Huang, Q.; Ni, H.; Li, X.; Ding, J.; Fu, H.; Li, Q. *Mater Res Appl* 2007, 1, 147.
11. Chen, N.; Wan, C.; Zhang, Y.; Zhang, Y. *Polym Test* 2004, 23, 169.
12. Sun, S.; Li, C.; Zhang, L.; Du, H.; Burnell-Gray, J. *Polym Int* 2006, 55, 158.
13. Tian, M.; Chen, G.; Guo, S. *Macromol Mater Eng* 2005, 290, 927.
14. Guo, Y.; Wang, M.; Zhang, H.; Liu, G.; Zhang, L.; Qu, X. *J Appl Polym Sci* 2008, 107, 2671.
15. Zhu, A.; Cai, A.; Zhang, J.; Jia, H.; Wang, J. *J Appl Polym Sci* 2008, 108, 2189.
16. Liang, Z.; Wan, C.; Zhang, Y.; Wei, P.; Yin, J. *J Appl Polym Sci* 2004, 92, 567.
17. Wan, C.; Tian, G.; Cui, N.; Zhang, Y.; Zhang, Y. *J Appl Polym Sci* 2004, 92, 1521.
18. Ren, J.; Huang, Y.; Liu, Y.; Tang, X. *Polym Test* 2005, 24, 316.
19. Wang, L.; Qin, Y.; Zhang, X. *Shanghai Plast* 2005, 1, 22.
20. Wang, J.; Zhang, Y.; Wang, H. *Mater Sci Technol* 2004, 12, 261.
21. Yang, M.; Dan, Y. *J Appl Polym Sci* 2006, 101, 4056.
22. Yang, M.; Dan, Y. *Colloid Polym Sci* 2003, 281, 794.
23. Mahdavian, A. R.; Ashjari, M.; Makoo, A. B. *Eur Polym J* 2007, 43, 336.
24. Tang, E.; Cheng, G.; Pang, X.; Ma, X.; Xing, F. *Colloid Polym Sci* 2006, 284, 422.
25. Zeng, Z.; Yu, J.; Guo, Z. *Macromol Chem Phys* 2005, 206, 1558.
26. Luo, Y.; Peng, L.; Dan, Y.; Zhang, L.; Zhao, K. *J Inorg Mater* 2007, 22, 499.
27. Blasse, G.; Rril, A. *Philips Res Rep* 1968, 23, 201.
28. Abbruscato, V. *J Electrochem Soc* 1971, 118, 930.