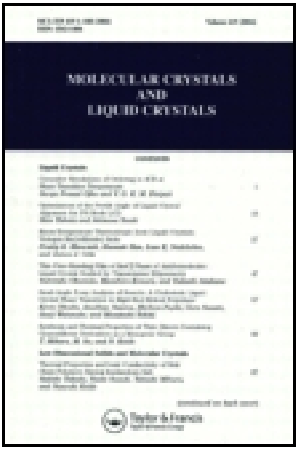

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Preparation and Characterization of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} Doped Polymer Composites

W. F. Wong [a], C. L. Mak [a], Y. W. Wong [a] & C. W. Hung [b]

[a] Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, PRC

[b] Great Wall Progress Company Limited, Winful Centre, Kwun Tong, Kowloon, Hong Kong SAR, PRC

Version of record first published: 23 Aug 2006

To cite this article: W. F. Wong, C. L. Mak, Y. W. Wong & C. W. Hung (2006): Preparation and Characterization of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} Doped Polymer Composites, Molecular Crystals and Liquid Crystals, 447:1, 223/[541]-232/[550]

To link to this article: http://dx.doi.org/10.1080/15421400500377230

Mol. Cryst. Liq. Cryst., Vol. 447, pp. 223/[541]–232/[550], 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500377230

Preparation and Characterization of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} Doped Polymer Composites

W. F. Wong
C. L. Mak
Y. W. Wong
Department of Applied Physics, The Hong Kong Polytechnic University,
Hung Hom, Kowloon, Hong Kong SAR, PRC

C. W. Hung
Great Wall Progress Company Limited, Winful Centre, Kwun Tong,
Kowloon, Hong Kong SAR, PRC

Long after-glow luminescent composites were fabricated by embedding phosphor $SrAl_2O_4$:Eu^{2+}, Dy^{3+} powders into polymethyl-methacrylate (PMMA) using solution casting and hot-press methods. In the first method, PMMA were dissolved in chloroform forming a homogenous solution and the phosphor powders were doped into the solution with different volume fractions. Transparent samples were obtained by air drying the solution in a container. Their optical properties were studied by transmittance measurement and emission spectroscopy. For tensile and impact tests, samples were obtained by pressing mixed phosphor and PMMA powders at 190°C. Based on these studies, the mechanical and optical properties of these composite were investigated.

Keywords: composites; long after-glow; mechanical and optical respectively

INTRODUCTION

ZnS:Cu phosphor has been well known as a long phosphorescent phosphor and used in variety of applications since last century. The popular use of phosphorescent was driven to enhance its after-glow brightness and longer decay time so that it can be used in diverse

---

This work was supported by Great Wall Progress Company Limited and the Innovation and Technology Fund (Grant No. UIT/55) of the Hong Kong SAR.

Address correspondence to W. F. Wong, Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, PRC. E-mail: 03901907R@polyu.edu.hk

applications. The combination of ZnS:Cu and radioisotopes were therefore developed to give better performance as result. However, the use of radioisotopes has been restricted because of safety and environmental considerations. Recently, a new type of long phosphorescent phosphor, $SrAl_2O_4$:Eu^{2+}, Dy^{3+}, with high brightness has been synthesized. Its brightness and decay time are almost ten times more than those of the conventional ZnS:Cu phosphor [1,2]. This new type of phosphor has good properties with no radioactive substances and harmless to environments. All these advantages together with its substantial high chemical stability lead to wide application of this material in industry. Unfortunately, these phosphors will lose their phosphorescent properties if they make contact with moisture. Therefore, incorporating these phosphors into plastic resins, which act as barriers, might retain their luminescent properties.

In this paper, long after-glow luminescent composites were fabricated by embedding phosphor $SrAl_2O_4$:Eu^{2+}, Dy^{3+} powders into polymethyl-methacrylate (PMMA) using solution casting and hot-press methods. Their optical and mechanical properties were measured using transmittance measurement, emission spectroscopy, tensile test and impact test. The effects of PMMA on the optical properties of the luminescent powders as well as the effects of the doped luminescent powders on the mechanical properties of PMMA were revealed.

EXPERIMENTAL

Luminescent composites of various doping concentrations, ranging from 0 vol% to 25 vol%, were fabricated by using solution casting and hot-press method. For solution casting method, bulk PMMA was firstly dissolved in chloroform to form a homogenous gel solution. The luminescent powders (Luminova, G300) were added into the solution according to the desired doping concentrations. Transparent samples of $100 \times 100 \times 3\,mm^3$ were prepared by air-drying the gel in a container. On the other hand, for the hot-press method, PMMA powder (Lucite) and the luminescent powder were mixed together using mechanical stirring. The mixed powder was then packed into the cavity of different moulds which were either dog-bone or edge-notched prismatic bar shapes. The mould was then placed in between parallel stainless steel plates wrapped in aluminum foil. The final stack was put in a hot-press machine (Carver 3856) and pre-heated at 190°C for 30 minutes without applying any pressure. A moderate pressure of 3000 pound per square inch was then applied for another 30 minutes while the temperature was kept at 190°C. The samples were finally cooled down to room temperature.

The crystallinity of the embedded powder was investigated by X-ray diffractometer (X'pert System, Philips) with Cu-K_α radiation. The excitation spectra, emission spectra and phosphorescence decay profiles were measured at room temperature using a SPEX spectrometer (Fluorolog). Samples fabricated by solution casting method were employed in our optical studies, as the samples obtained by solution casting usually possess a better transparency as compared to those obtained by hot-press method. Durability of the phosphorescence of the luminescent composites was investigated by immersing the samples in water for various durations, and their emission spectra as well as decay curves were then measured.

The samples for the tensile test were dog-bone shapes of $60 \times 10 \times 3\,\mathrm{mm}^3$. For each doping concentration, five tensile tests [3] were carried out at a displacement rate of 1 mm/min using a Lloyd I Instruments (LR 30 K) with M2 self-tightening wedge grips. Data of all the tensile tests performed were collected, stored and averaged, and presented graphically as a single stress – strain curve representative of a particular group of samples of a given doping concentration. For impact test, the samples were single edge-notched prismatic bar shapes of $63.5 \times 13 \times 3\,\mathrm{mm}^3$. Charpy impact tests were carried out in 3-point flexure using a Zwick impact tester with a 2 J hammer. The notch length corresponded to a ratio of notch length/specimen depth of 2:10. A minimum of five broken specimens were required for a given doping concentration, as recommended by the ASTM standard [4].

RESULTS AND DISCUSSION

Optical Properties

Figure 1 shows the XRD θ-2θ scan patterns of the luminescent composites. The XRD scan patterns of pure PMMA and luminescent powder are also shown for comparison. In Figure 1, it was noticed that the crystallinity of the embedded powder was not altered when doped into PMMA matrix. This indicates that the luminescent powder is only physically mixed with the polymer. Therefore, we expect that the luminescent properties of the powder should be preserved inside the PMMA matrix.

The excitation and emission spectra of pure luminescent powder and the luminescent composite of 7.6 vol% are shown in Figure 2. The excitation and emission peaks are located at 370 nm and 515 nm respectively. The excitation and emission profiles of the luminescent composites have no observable changes when embedded in PMMA matrix.

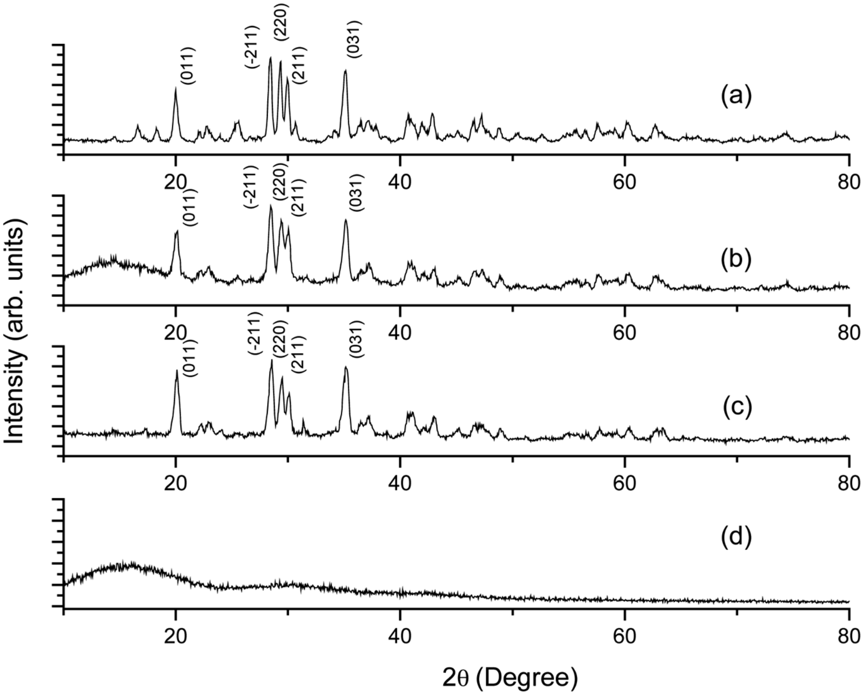

FIGURE 1 XRD patterns of (a) pure luminescent powder, luminescent composites of (b) 18.1 vol% and (c) 1.7 vol%, and (d) virgin PMMA.

Afterglow decay curves of pure luminescent powder and the luminescent composite of 7.6 vol% doping are shown in Figure 3. Both samples showed long afterglow properties when they were excited by UV light (397 nm). When the light source was switched off after exciting for 40 min, the intensity of the afterglow decreased as expected. As shown in Figure 3, pure luminescent powder exhibited a longer afterglow property than the luminescent composite by comparing the decay time constant.

The effect of the doping concentration on the emission intensity of the composites was investigated. Samples of different doping volume fraction were excited at 397 nm and monitored at 517 nm. All the samples had the same dimension and the excitation intensity was kept constant. The emission intensity as a function of doping concentration is shown in Figure 4. To our surprise, it was found that the emission intensity peaks at about 12.4 vol% fraction. In general, emission intensity increases with small doping concentration and saturates at

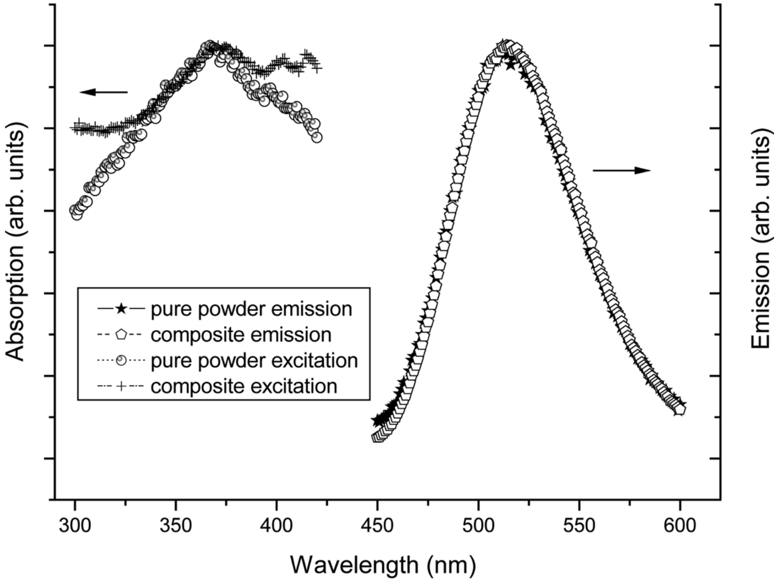

FIGURE 2 Excitation and emission spectra of pure luminescent powder and luminescent composite of 7.6 vol%.

some doping concentration. Our results show that for doping concentration larger than 12.4 vol%, the emission intensity drops. We repeated the measurements with different set of samples. Similar results were obtained. This maximum might probably due to the reabsorption effect between the luminescent powders. Further studies will be needed to reveal this unexpected property.

The effect of moisture on the luminescent properties of the embedding luminescent powder was investigated by immersing the luminescent samples in water for different durations. Figure 5(a) shows the normalized intensity of the luminescent composites as a function of immersing time. The emission intensity drops to about 60% of original after 50 days. Compared with Figure 5(b) where the emission intensity of the pure powder drops to only about 10% of original after 5 days, we believe that PMMA matrix significantly reduces the deterioration rate of the luminescent powders.

Mechanical Properties

Figure 6 shows the tensile strength values for composites of different doping concentrations. In general, the tensile strength of all

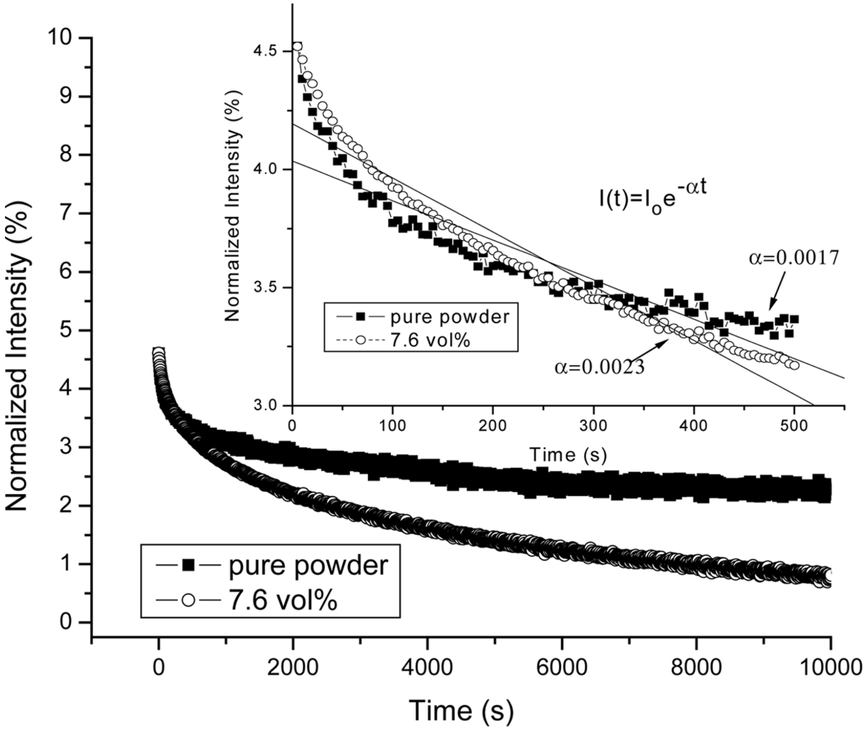

FIGURE 3 Afterglow emission of powder and composite (7.6 vol%) after illumination under 397 nm UV light for 40 minutes and monitored at 517 nm. I/I_o is the normalized intensity and α is the decay constant.

composites decreases with increasing phosphor content, indicating that the luminescent powder acts as non-reinforcing filler. A possible explanation for the decrease might be due to the low interfacial interaction between the embedding powders and PMMA. This low interaction leads to mechanical rupture at the PMMA interface.

Figure 7 shows that the elongation at break decreases with increasing luminescent powder content. In the fabrication process, the addition of a different phase (luminescent powders) to a polymer matrix material usually significantly decreases the elongation at break.

Figure 8 plots the dependence of the impact energy as a function of doping concentration. The impact resistance is, in general, increased with the doping concentration and peaked at volume fraction of 12.4%. It then slightly drops with further increase of the phosphor

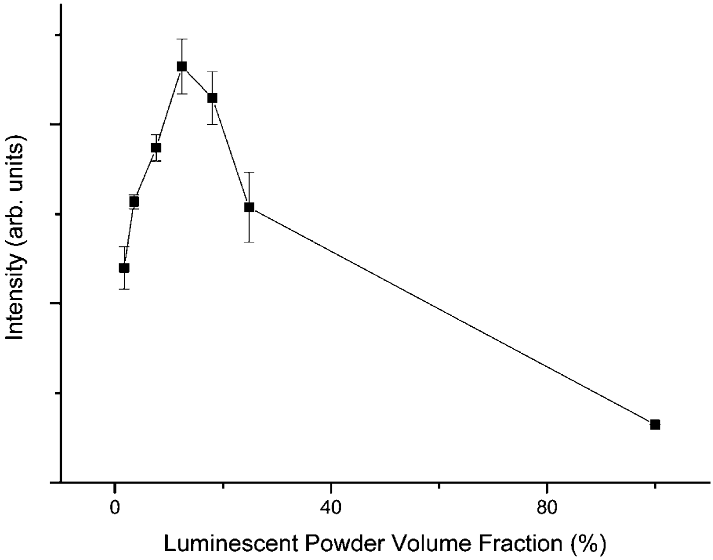

FIGURE 4 Emission intensity as a function of doping volume fraction.

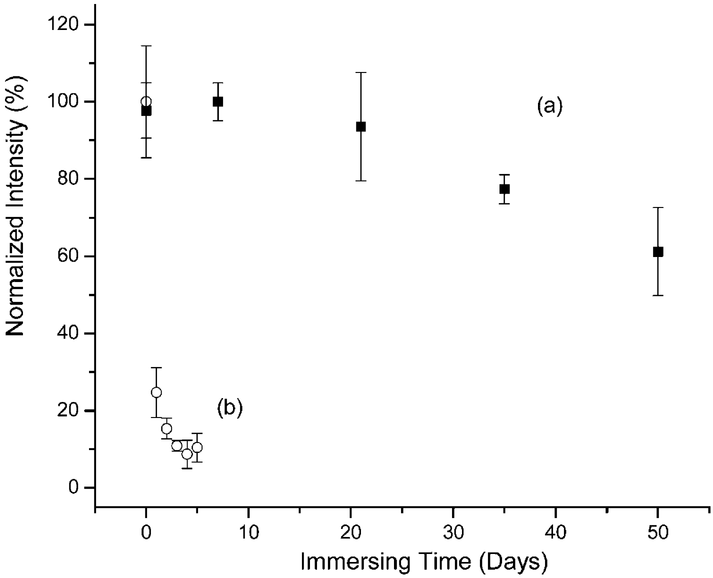

FIGURE 5 Emission intensity of (a) luminescent composite (7.6 vol%) and (b) pure powder, excited at 397 nm and monitored at 517 nm after immersing in water.

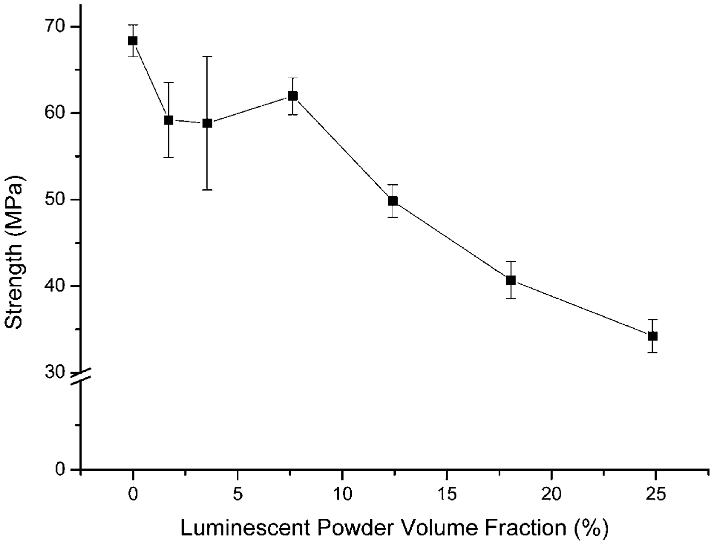

FIGURE 6 Tensile strength of luminescent composites of different doping concentrations.

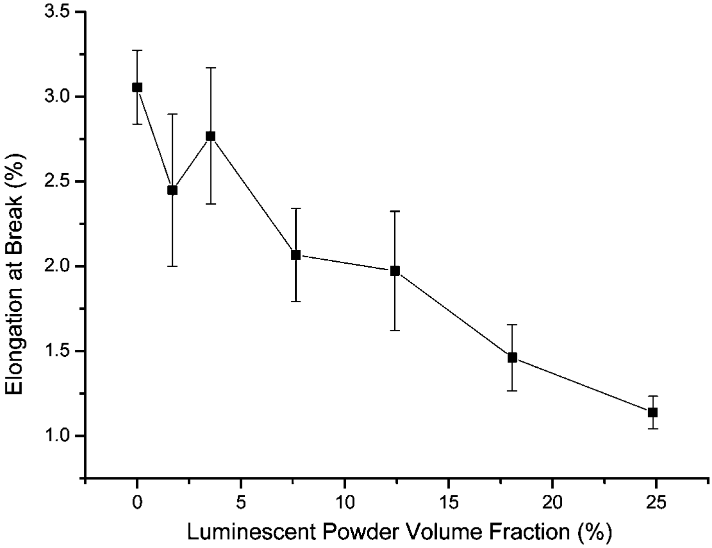

FIGURE 7 Elongation at break for luminescent composites with different doping concentrations.

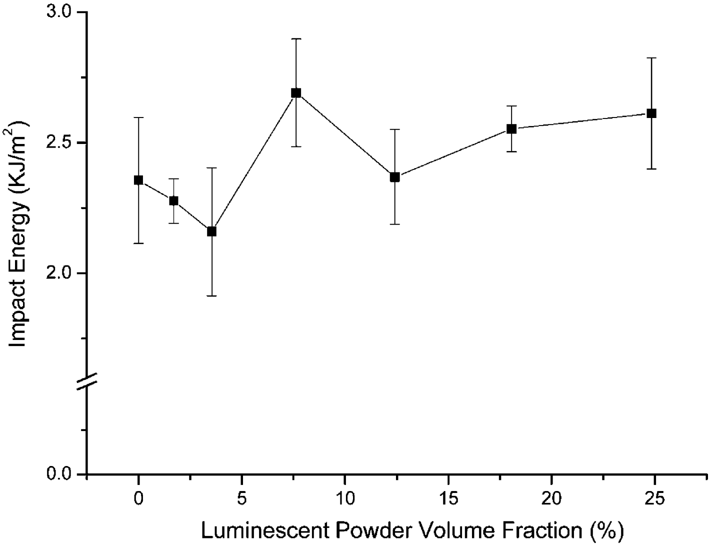

FIGURE 8 Toughness of PMMA/luminescent powder composites showing a peak at 12.4 vol%.

content. The increase in impact energy might be due to the fact that matrix phase of the composite transmits and distributes the external applied stress to the luminescent powder which enhances the impact strength.

CONCLUSIONS

Homogeneously PMMA/luminescent powder composites were fabricated and the variations of optical and mechanical properties were investigated as a function of doping concentration. The excitation and emission spectra of composite has a similar profile with pure phosphors. The decay property of pure phosphor is slightly better than that of composite. 12.4 vol% doping concentration has the highest luminescent emission intensity. The composite maintains a luminescent intensity larger than half of its initial value after immersing under water for 50 days. In the mechanical properties, both tensile strength and elongation at break slightly decrease with increasing phosphor content. However, impact resistance is improved with increasing phosphor content upto 12.4 vol%.

REFERENCES

[1] Matsuzawa, T., Aoki, Y., Takeuchi, N., & Murayama, Y. (1996). A new long phosphorescent phosphor with high brightness $SrAl_2O_4:Eu^{2+}$, Dy^{3+}. *J. Electrochem. Soc.*, *143*, 2670.

[2] Yamamoto, H. & Matsuzawa, T. (1997). Mechanism of long phosphorescence of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} and $CaAl_2O_4:Eu^{2+}$, Nd^{3+}. *J. Luminescence*, *72–74*, 287.

[3] Standard Test Methods for Tensile Properties of Plastics, ASTM D638–03.

[4] Standard Test Methods for Determining the Charpy Impact Resistance of Notched Specimens of Plastics, ASTM D6110–04.