

Effect of Y₂O₃:Eu³⁺ Particles on Fluorescence, Thermal and Mechanical Properties of Poly(methyl methacrylate) Composite†

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In order to obtain photoluminescence characteristics of poly(methyl methacrylate) (PMMA), $Y_2O_3:Eu^{3+}$ particles are modified by silane coupling agent (KH-151) and introduced into poly(methyl methacrylate) *via* the *in situ* polymerization. The $Y_2O_3:Eu^{3+}$ /PMMA composites exhibit enhanced properties of strength, thermal stability and fluorescence comparing with poly(methyl methacrylate). In particular, the $Y_2O_3:Eu^{3+}$ /PMMA composite with 0.3 wt % content of $Y_2O_3:Eu^{3+}$ exhibits the highest tensile strength of 55 MPa, suggesting its potential application in photoluminescence.

Keywords: Y₂O₃:Eu³⁺, Poly(methyl methacrylate), Particles, Polymerization.

INTRODUCTION

Metal oxide-polymer composites which combine the desired functionalities of both polymer matrix and metal oxide fillers have attracted much attention in recent years. Europium-doped Y_2O_3 (Y_2O_3 :Eu³⁺) is considered as an important fluore-scent material owing to its good luminescent property with high chemical stability and acceptable atmospheric stability that give rise to many application areas, such as fluorescent lights, plasma display panel (PDP), cathode ray tubes (CRT) and field emission display (FED)^{1,2}. Hence, Y_2O_3 :Eu³⁺ particles are usually introduced into polymer matrix to improve the fluorescent property of polymer.

Poly(methyl methacrylate) (PMMA) is an optically clear amorphous thermoplastic polymer with excellent impact strength and dimensional stability. Due to its favorable properties, PMMA is an excellent substitute for conventional inorganic glass in many applications. Herein, we choose PMMA as polymer base and synthesize $Y_2O_3:Eu^{3+}/PMMA$ composites by *in situ* bulk polymerization. Their fluorescence, thermal and mechanical properties are investigated in details.

EXPERIMENTAL

Y₂O₃:Eu³⁺ particles were prepared according to the following procedure. Yttrium oxide and europium oxide were dissolved in dilute hydrochloric acid with constant stirring and then sodium hydroxide solution was added to adjust the pH value of the system to 13. The mixture was dried at 160 °C in a vacuum oven for 6 h and then calcined at 900 °C for 4 h. The final product was ground into powder and treated with the silane coupling agent (KH-151) under reflux for 4 h at 80 °C.

 $Y_2O_3:Eu^{3+}/PMMA$ composites were synthesized as follow: various amounts of $Y_2O_3:Eu^{3+}$ particles 0, 0.1, 0.3, 0.5, 0.7 and 0.9 % (wt %) were dispersed into methyl methacrylate monomer by sonicating. Polymerization of this mixture was initiated by azodiisobutyronitrile (AIBN) under constant stirring at 80 °C for 0.5 h. Afterwards, the solution in the flask was poured into a glass mould and kept at 50 °C for 5 h and subsequently at 100 °C for 2 h in an electric oven.

RESULTS AND DISCUSSION

FTIR spectra of modified $Y_2O_3:Eu^{3+}$ particles (a) and $Y_2O_3:Eu^{3+}/PMMA$ composite (b) are shown in Fig. 1. The absorption peaks between 3400 and 3450 cm⁻¹ are associated with -OH groups, which are bonded onto the surface of $Y_2O_3:Eu^{3+}$ particles. The characteristic peak of C=C at 1620 cm⁻¹ in Fig. 1(b) disappears, suggesting that PMMA chains graft onto *m*- $Y_2O_3:Eu^{3+}$ particles successfully. Additionally, two characteristic bands of acetate groups centered at 1660 and 1260 cm⁻¹ are attributed to the stretching vibrations of C=O and C-O in PMMA, respectively.

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Fig. 2 shows the fluorescence spectra of Y_2O_3 : Eu³⁺/PMMA composites after excitation at 254 nm. All fluorescence spectra of Y₂O₃:Eu³⁺/PMMA composites show red emission centered at 605-620 nm which is assigned to 4f-electronic transitions of Eu³⁺ (⁵D₀-⁷F₂ electric dipolar transition)^{3,4}. Additionally, their fluorescence intensities increase with increasing Y2O3:Eu3+ content.



Fluorescence spectra measured under the 254 nm UV excitation of Fig. 2. Y₂O₃:Eu³⁺/PMMA 0.1 % (a), Y₂O₃:Eu³⁺/PMMA 0.3 % (b), $Y_2O_3:Eu^{3+}/PMMA~0.5~\%$ (c), $Y_2O_3:Eu^{3+}/PMMA~0.7~\%$ (d) and Y₂O₃:Eu³⁺/PMMA 0.9 % (e)

Fig. 3 shows the dependence of the tensile strength of Y_2O_3 :Eu³⁺/PMMA composites on Y_2O_3 :Eu³⁺ contents. The result shows that the tensile strength first increases to a maximum of 55 MPa when Y_2O_3 : Eu³⁺ content increase to 0.3 %, then it starts to decrease as Y₂O₃:Eu³⁺ content increasing. It should be noted that all composites exhibit better mechanical performance than pure PMMA. The highest tensile strength of Y₂O₃:Eu³⁺/PMMA composites measured in this study are 38 % higher than pure PMMA.



Fig. 3. Effect of Y₂O₃:Eu³⁺content on the tensile strength of Y₂O₃:Eu³⁺/ PMMA composites

Thermogravimetric analysis (TGA) of pure PMMA and Y_2O_3 : Eu³⁺/PMMA composites are shown in Fig. 4. Apparently, thermal stability of the composite is significantly improved by incorporating Y₂O₃:Eu³⁺particles into PMMA matrix. They are thermally stable up to 180 °C and start to degrade in threesteps. The thermal degradation of the Y₂O₃:Eu³⁺/PMMA composites shifts to higher temperature comparing with pure PMMA, especially at high content of Y_2O_3 :Eu³⁺ (0.5 wt %), confirming the enhancement of thermal stability of PMMA by Y₂O₃:Eu³⁺ particles.



Fig. 4. TGA curves of pure PMMA and Y₂O₃:Eu³⁺/PMMA composites

Conclusion

Red emitting Y₂O₃:Eu³⁺/PMMA composites with excellent thermal stability and tensile strength were synthesized by in situ bulk polymerization. Tensile strength and TGA data suggest that mechanical and thermal stability are dependent on Y₂O₃:Eu³⁺ content. The optimized Y₂O₃:Eu³⁺/PMMA composites with favorable luminescent and mechanical properties holds promising as a new class of fluorescent material.

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