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ORIGINAL CONTRIBUTION

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The study of preparation and luminescence of polymethyl methacrylate/rare earth composite luminescent materials

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Abstract The alkaline-earth–rare-earth–aluminate systems phosphors are the new types of phosphors, which process very bright, safer, and excellent photoluminescence. Because of hydrolysis, however, the capacity of luminescent materials will fall down and the use value of luminescent materials will also be lost. Water-resistant polymers, which can form a kind of water-resistant clad on the surface of luminescent material powder, will solve this problem and the significance of its application is important. In this study, the polymethyl methacrylate (PMMA)/rare earth composite luminescent materials were prepared through grafting emulsion polymerization of methyl methacrylate onto the surface of luminescent materials. To study the structure and properties of the PMMA/rare earth composite luminescent materials, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and photoluminescent properties were measured. From the curves of FTIR and TGA, we can find that the organic parts are attached with the inorganic parts in the PMMA/rare earth composite luminescent materials. The results of luminescent decay curves show that the resistance to water of the PMMA/rare earth composite luminescent materials is much better than that of the unmodified luminescent materials because the organic parts had been grafted on the luminescent materials.

Keywords Polymethyl methacrylate · Rare earth · Luminescent materials · Emulsion polymerization

Introduction

The visible-light-generating components of emissive, full-color, flat-panel displays are called phosphors. Phosphors are composed of an inter-host lattice and an optically excited activator, typically a 3d or 4f electron metal. Inorganic materials, such as silicate, phosphate and aluminate, activated by rare earth ions are important types of photo-luminescence phosphors for their excellent luminescent properties as reported by Forelich in 1946. The luminescent property of the alkaline-earth–rare-earth–aluminate systems is created by the stimulated absorption transition of electron of rare earth ions in different orbital. For the excellent properties of this kind of phosphors, for example excellent photoresistance and long-lasting photoluminescence with no radiation [1], those materials which contain rare earth ions as dopants have attracted much attention due to their strong photoluminescence [2, 3]. The Eu^{2+}-doped alkaline earth aluminates, $SrAlO_2$, are efficient yellow/green-emitting persistent luminescent materials for laser application, extending from the ultraviolet to the near-infrared, and have been used in many fields as fire protection, military affairs, and technologies. Because of inorganic materials as host material, however, the luminescent properties of host alkaline earth metals also show some deficiencies, e.g., the handicap of water-resistant capacity, which limit the application of those materials. To improve their capacities, polymer/rare earth composite materials have been researched [4–6]. Those materials have been prepared mostly by two methods, including doping and bonding methods. The latter one

focuses on chemical linkage; just a reverse, the former one depends on physical linkage. Bonding-type rare earth polymers are advantageous compared with doping-type rare earth polymers. Such advantage has been related to the better product quality and good consistency between inorganic parts and organic parts. It is an efficient technique for the preparation of polymer/rare earth composite materials due to good consistency of the reagents and relatively stabile chemical property, which results in more processing capability than those obtained by directly adulterating method. Using doping method, the control of the way of linkage between phosphor and polymer and the affection of luminescent properties for types of resins are extremely difficult. In some studies [7–9], researchers have investigated that the existence of resin affected the luminescence properties. In this paper, emulsion polymerization is employed to prepare polymethyl methacrylate/rare earth composite materials. The photoluminescent properties of the composite materials are compared to those of the unmodified luminescent materials.

Experimental

Materials

Methyl methacrylate (MMA) from Chengdu Kelong Chemical Reagents Factory (Chengdu, China), used in the synthesis process, was purified before use by distillation under reduced pressure. $NaHCO_3$ solution (1%) was used to control the pH of the dispersions and $NaHCO_3$ was received from Shanghai Waigang No. 2 Chemical Reagent Factory (Shanghai, China). The initiator, potassium peroxydisulfate (KPS), and sodium lauryl sulfate (SDS), which were supplied by Beijing Chemical Reagent Factory (Beijing, China), were of analytical grade and used without further purification. The coupling agent ([3-(trimethoxysily) propyl methacrylate]) was of reagent grade and used as received. The luminescent materials were $SrAl_2O_4$ phosphors; the alkaline earth aluminates were used as host materials in which and they came from Sichuan Xinli Industrial Group (Chengdu, China). The ethanol and polyvinyl alcohol (PVA) used in this work were available commercially. Water was deionized before use.

Preparation of the PMMA/rare earth composite luminescent materials

Modification of the luminescent materials

Before polymerization, the luminescent materials of host alkaline earth aluminate were modified in coupling agent (3-(trimethoxysily) propyl methacrylate) ethanol solution and dried at 73~85 °C to remove the ethanol. The amount of coupling agent used to modify the luminescence materials was 8% of the amount of the luminescent materials. Then the products containing some coupling agent, which did not react with hydroxyl groups on the surface of luminescent materials, were extracted with ethanol (99.7%) for several days in a Soxhlet extractor and dried at 70~80 °C to remove the solvent.

Preparation of the PMMA/rare earth composite luminescent materials

The PMMA/rare earth composite luminescent materials were prepared through grafting emulsion polymerization of MMA onto the surface of luminescent materials. Firstly, the SDS, PVA, and $NaHCO_3$ aqueous solution were charged successively in a five-neck autoclave treated under reflux at 50~60 °C with stirring. When the aqueous solution turned clear aqueous solution, luminescent materials and KPS aqueous solution were added to this suspension. After a time, purified MMA was slowly added dropwise under stirring until pH value reached 7.5. Then, emulsion polymerization was carried out at 70~80 °C for about 4 h. The products obtained were filtered, washed with deionized water to remove the emulsifier, dried, and crushed. After that, the PMMA/rare earth composite luminescent materials were obtained.

Characterization techniques

TGA measurement

The unmodified luminescent materials, the luminescent materials only modified by coupling agent, and the PMMA/rare earth composite luminescent materials were characterized by thermogravimetric analysis (TGA). For the thermal analysis, 6~10 mg of materials were placed in Al_2O_3 crucibles and heated at a rate of 10 °C/min in a synthetic airflow of 50 ml/min. TGA measurement was simultaneously performed in the range of 20–700 °C.

FTIR measurement

The transformation of organic parts in the chemical structure of all the samples was analyzed using Fourier transform infrared spectroscopy (FTIR), using a Nicolet-560 FTIR spectrometer. Before the FTIR measurement, the PMMA/rare earth composite luminescent materials were extracted with chloroform (99.0%) for several days in a Soxhlet extractor to remove PMMA which was only attached with the PMMA/rare earth composite materials by weak bond. During extracting, the chloroform solution was replaced by chloroform (99.0%) after an interval time. After those steps, the samples were dried and pretreated in the form of KBr pellets.

Luminescent property measurement

The luminescent decay curve of intensity with time of luminescent materials was recorded with the apparatus for testing photo-luminescence (PR-305).

The measurement of resistance-to-water property of luminescent materials

Because of luminescent materials hydrolyzing in water, the pH value of aqueous solution of the unmodified luminescent materials would show an obvious increment so, in this study, we measured the pH value by pH reagent paper to conclude the resistance-to-water property of luminescent materials.

Results and discussion

Structural analysis

Before polymerization with MMA, the luminescent materials were modified in 3-(trimethoxysily) propyl methacrylate ethanol solution. The 3-(trimethoxysily) propyl methacrylate has silanol groups which can react with hydroxyl groups on the surface of luminescent materials and other groups which can react with MMA in emulsion polymerization. So it can be inferred that the polymer parts and inorganic parts in the PMMA/rare earth composite luminescent materials are attached by a bond, which has strong intermolecular interaction.

To confirm this inference, the PMMA/rare earth composite luminescent materials were extracted by chloroform (99.0%). During the process, the PMMA, which only blended with the PMMA/rare earth composite luminescent materials, was removed easily. The FTIR and TGA technologies were used to characterize the structure of the PMMA/rare earth composite luminescent materials.

During the time when the products were being extracted, the chloroform solution was replaced by chloroform (99.0%) at the interval time and the FTIR spectrum of chloroform solution, used to remove the PMMA, was measured at a different time. Until the results did not show the characteristic absorption of carbonyl group (>C=O) of PMMA, we can confirm that the PMMA had been removed from the PMMA/rare earth composite luminescent materials absolutely. The FTIR spectra of chloroform (99.0%), the chloroform solution after extracting the samples for 4 and 52 h, respectively, are shown in Fig. 1.

The FTIR spectrum of the chloroform solution after extracting for 4 h (Fig. 1c) shows characteristic absorption of the >C=O group of PMMA at 1,730.85 cm^{-1} and of C-O-C at 1,300~1,190 cm^{-1}, compared with the spectrum of chloroform (99.0%) (Fig. 1a). That result may indicate that there is still some free PMMA in the PMMA/rare earth composite luminescent materials. In Fig. 1a,c, however, only the characteristic absorption bands of $>CH_2$ at about 3,020.61 cm^{-1} and that of C-Cl from chloroform at about 1,215.62 and 759.56 cm^{-1} can be found, respectively, while the band centered at about 1,730 and 1,300~1,190 cm^{-1}, which is due to the ester group stretching that cannot be observed. So, it can be inferred that the PMMA, only blending with the PMMA/rare earth composite luminescent materials, has been removed absolutely by extracting for 52 h.

Figure 2 shows the FTIR spectra of the unmodified luminescent materials, the PMMA, and the extracted PMMA/rare earth composite luminescent materials. To compare the relative intensity of the band in wave number

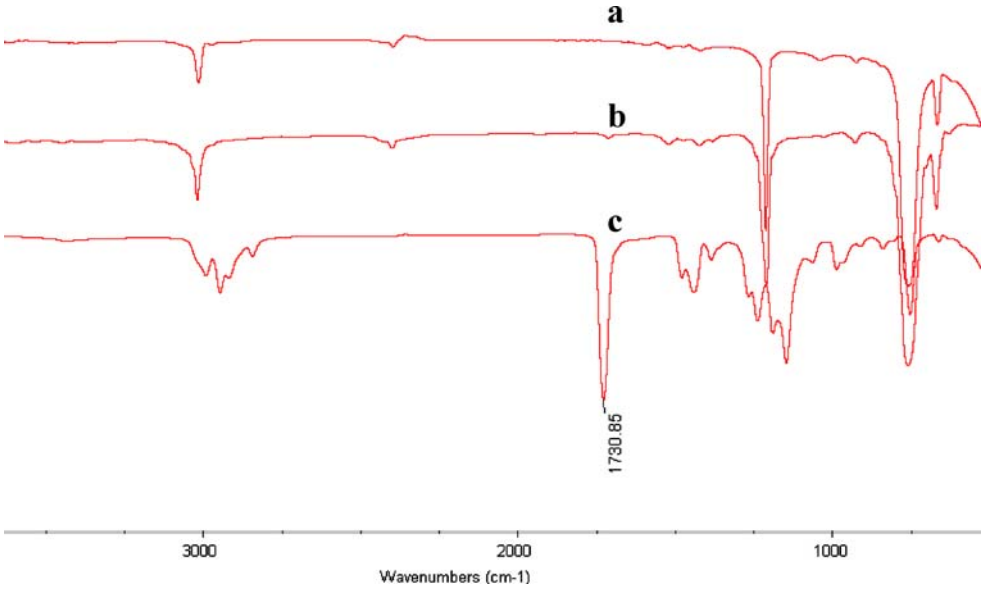

Fig. 1 FTIR spectra of **a** chloroform (99.0%), **b** the chloroform solution after extracting sample for 52 h, and **c** the chloroform solution after extracting sample for 4 h

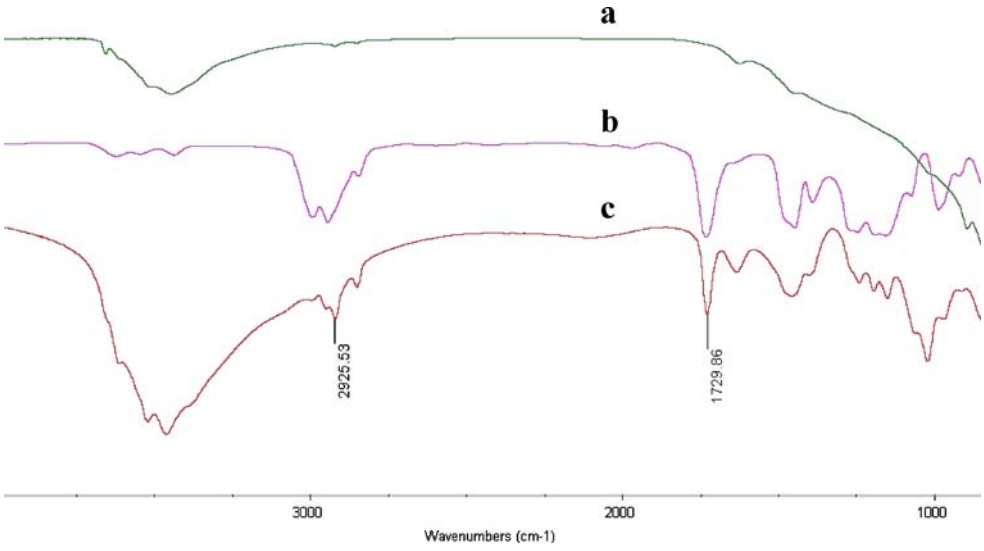

Fig. 2 FTIR spectra of **a** the unmodified luminescent materials, **b** the PMMA, and **c** the extracted PMMA/rare earth composite luminescent materials

region at 3,800~1,000 cm^{-1}, the absorption intensity of spectra shown in Fig. 2 is normalized to the peak intensity of >C=O group stretch. From the FTIR spectrum of the PMMA/rare earth composite luminescent materials (Fig. 2c), we can find the presence of absorption at 1,730 cm^{-1}, which is attributed to the carbonyl group (>C=O), and the appearance absorption at 2,924.64 and 2,854.13 cm^{-1}, which are assigned to the asymmetric and symmetric stretching of methylene (>CH_2) bands, respectively. The FTIR spectrum of the unmodified luminescent materials (Fig. 2a) shows no characteristic absorption of >C=O group at about 1,720 cm^{-1} and of >CH_2 group at about 2,900 cm^{-1}. The FTIR spectrum of the PMMMA/rare earth composite luminescent materials (Fig. 2c) shows that the shape of the characteristic band of >C=O group stretch is much similar to that of >C=O group stretch mode of the PMMA (Fig. 2b). Because the PMMA, only blending with the PMMA/rare earth composite luminescent materials, has been removed absolutely, the characteristic peak of >C=O group appearing in Fig. 3c comes only from the organic parts of PMMA/rare earth composite luminescent materials. These results support that the PMMA chain has attached with the inorganic luminescent materials by a stronger bond.

After modifying the luminescent materials, the 3-(trimethoxysily) propyl methacrylate was entailed on the surface of luminescent materials by the reaction between silanol groups and hydroxyl groups, and other groups in the coupling agent can react with MMA in emulsion polymerization. We can presume that PMMA was grafted onto the surface of luminescent materials across coupling agent. As the ratio (3.680:1) of area of characteristic absorption peak of the carbonyl group (>C=O) to that of methylene (>CH_2) in Fig. 2b was higher than the ratio (1.588:1) of area of characteristic absorption peak of carbonyl group (>C=O) to that of methylene (>CH_2) in Fig. 2c, the characteristic absorption bands of >C=O in the FTIR spectrum of the PMMA/rare earth composite luminescent materials may be not only from PMMA.

To prove this assumption, the unmodified luminescent materials, the coupling agent, and the PMMA/rare earth composite luminescent materials were measured further by FTIR spectroscopy and the FTIR spectra are shown in Fig. 3. By comparing the FTIR spectrum of the PMMMA/rare earth composite luminescent materials (Fig. 3c) and the FTIR spectrum of the coupling agent (Fig. 3b), it can be seen that the ratio (1.096:1) of area of characteristic absorption peak of >C=O group to that of >CH_2 in Fig. 3b is lower than the ratio (1.588:1) of area of characteristic absorption peak of carbonyl group (>C=O) to that of methylene (>CH_2) in Fig. 3c. The characteristic absorption of >C=O group at about 1,720 cm^{-1} and of >CH_2 group at about 2,900 cm^{-1} cannot be found in the FTIR spectrum of the unmodified luminescent materials (Fig. 3a). The results further indicate that the PMMA molecules are attached with the luminescent materials across a coupling agent.

From the difference between the two TGA curves of the unmodified luminescent materials (Fig. 4a) and the PMMA/rare earth composite materials (Fig. 4b), we can further study the structure of the PMMA/rare earth composite materials. From Fig. 4a, it can be seen that about 1 wt% weight loss is observed in the temperature range from about 50 to 95 °C, implying that the gas absorbed on the surface of the unmodified luminescent materials is removed efficiently. About 1.7 wt% weight loss is observed at about 260 °C due to the loss of water absorbed by the physical bond, and the decomposition of hydroxyl group on the surface of unmodified luminescent materials occurred between 300 and 600 °C. The TGA curve of the PMMA/rare earth composite luminescent materials (Fig. 4b) shows that there are about 20 wt% weight loss from 100 to 600 °C, much higher than the weight loss of the unmodified luminescent materials which is only about 2 wt%. The higher weight loss of the PMMA/

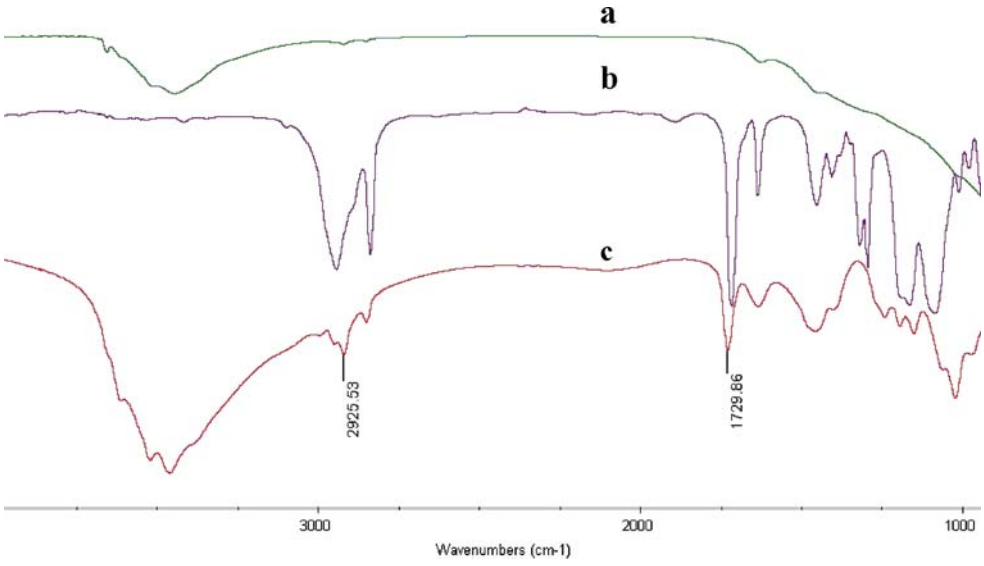

Fig. 3 FTIR spectra of **a** the unmodified luminescent materials, **b** the coupling agent, and **c** the extracted PMMA/rare earth composite luminescent materials

rare earth composite luminescent materials comes from the vaporization and decomposition of organic part of the composite luminescent materials. The different amount of weight loss between the unmodified luminescent materials and the PMMA/rare earth composite luminescent materials further indicates that the PMMA has been entailed on the surface of the luminescent materials.

Resistance-to-water property of luminescent materials

It is well known that, in $SrAl_2O_4$ phosphor, Eu^{2+} ions are the luminescent centers [10], the photo-excited luminescence is considered to be the transition from 5d level to 4f level of Eu^{2+}, and holes in the traps are responsible for the long afterglow. In the present system, it is the hole trapped–transported–detrapped process that results in the properties of long afterglow of $SrAl_2O_4$:Eu^{2+} phosphor. During the process, the alkaline earth aluminate played an important role. But after soaking in water for a time, the $SrAl_2O_4$, as the host material of luminescent materials, is easily

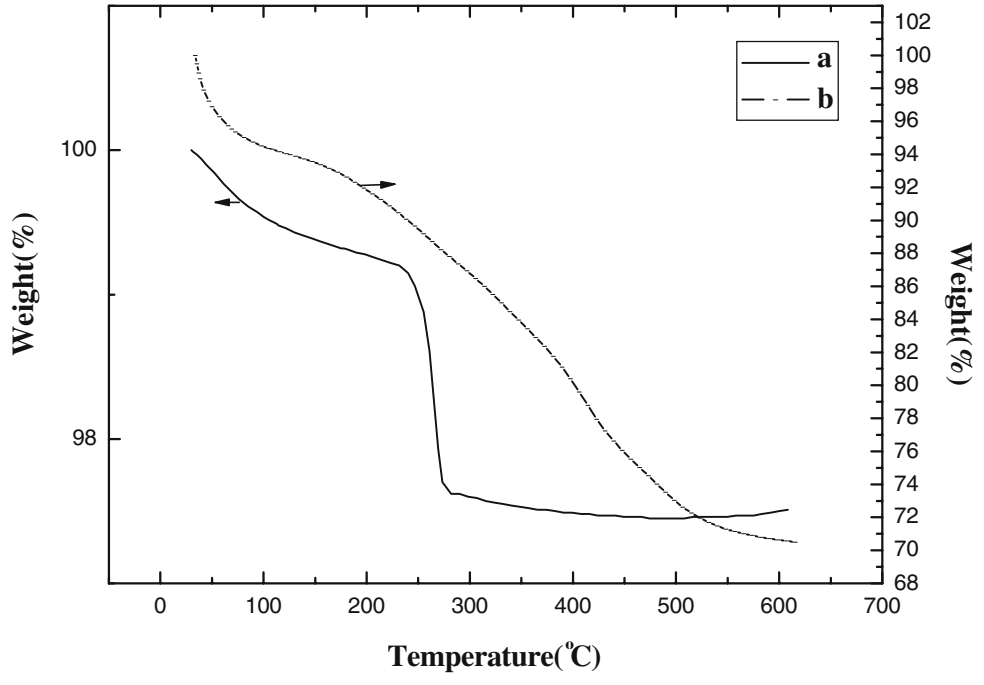

Fig. 4 TGA curves of **a** the unmodified luminescent materials and **b** the PMMA/rare earth composite materials

hydrolyzed, and the defects dispersed on the surface of $SrAl_2O_4$ phosphors decrease, resulting in the relative luminescent properties of those phosphors falling down. The process of this reaction is described in Scheme 1.

$$SrAl_2O_4 + 4H_2O \rightarrow Sr^{2+} + 8OH^- + Al^{3+}$$

Scheme 1 Schematic diagrams of hydrolyzation of $SrAl_2O_4$

We know that the rare earth ions are very sensitive to the atomic environment and can act as a probe to provide insight into the local structural details. It can thus be assumed that the internal characteristic of the particle possesses a more regular order. If the defects on the surface of luminescent materials are broken and the regular order is damaged, the capacity of luminescence will fall down and the use value of luminescent materials also will also be lost. From Scheme 1, we can find that the host materials of $SrAl_2O_4$ are broken, the regular order is damaged and the amount of OH^- increases due to the hydrolyzation, resulting in that the pH value of aqueous solution increases with the time increasing. So the excellent resistance-to-water property of the luminescent materials can protect the host materials from hyrodlyzation and improve processing capacity of luminescent materials. The change of pH value of aqueous solution of luminescent materials reflects the resistance-to-water property of luminescent materials. To study the resistance-to-water property of the PMMA/rare earth composite luminescent materials, the unmodified luminescent materials and the PMMA/rare earth composite luminescent materials have been soaked in water for a time and the pH values are measured after an interval of the same time.

We can infer the different resistance-to-water property of the unmodified luminescent materials and the PMMA/rare earth composite luminescent materials from Fig. 5. The pH curve of aqueous solution of the unmodified luminescent materials (Fig. 5a) indicates that the pH value increases very fast, changing from 8 to 12.5 in 500 min. On the contrary, the pH value of aqueous solution of the PMMA/rare earth composite luminescent materials in Fig. 5b changes very slowly and smoothly, only changing from 5.5 to 6 in 300 min, and always keeps the constant pH value of 6 after 300 min. As shown in Scheme 1, the unmodified luminescent materials has hydrolyzed during soaking in water, which may result in the relatively more amount of OH^- and in making the quickly increasing pH value of aqueous solution behave (Fig. 5a). The PMMA/rare earth composite luminescent materials, however, hardly hydrolyzed after soaking in water and the change in pH value of aqueous solution shows a very slow and flat trend (Fig. 5b) because of the organic parts forming a kind of water-resistant clad on the surface of luminescent materials powders. The results are consistent with that of FTIR and TGA measurements and further prove the PMMA being grafted on the surface of the rare earth luminescent materials.

The resistance-to-water property affects the luminescent intensity of luminescent materials after soaking in water for

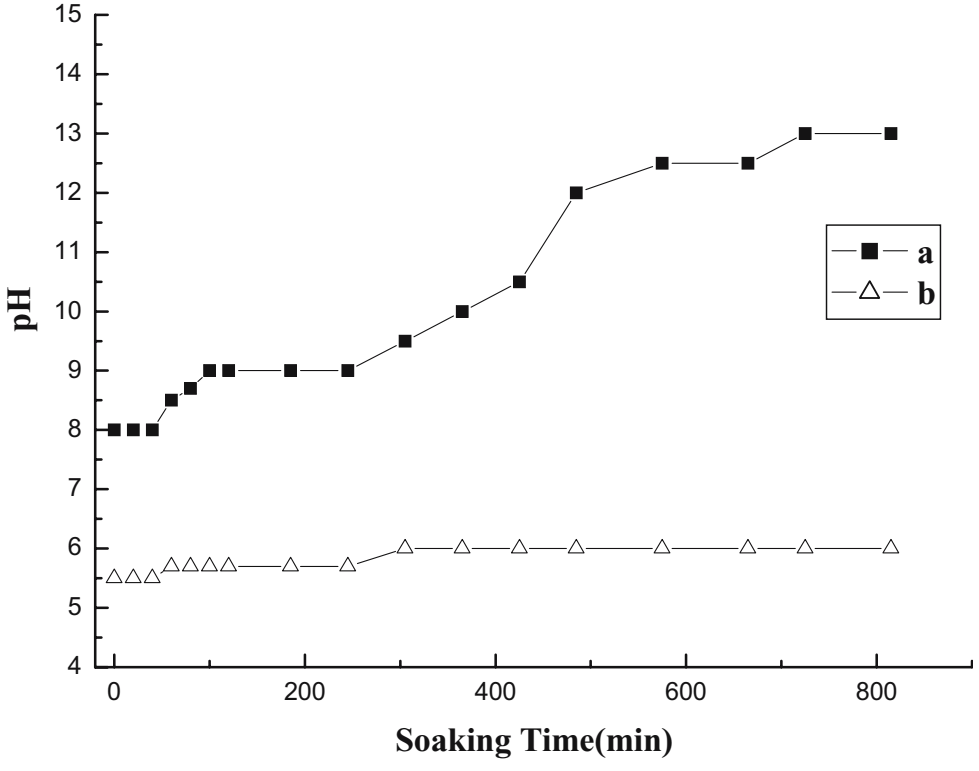

Fig. 5 The pH curves of two kinds of phosphors after soaking in water of **a** unmodified luminescent materials and **b** PMMA/rare earth composite luminescent materials

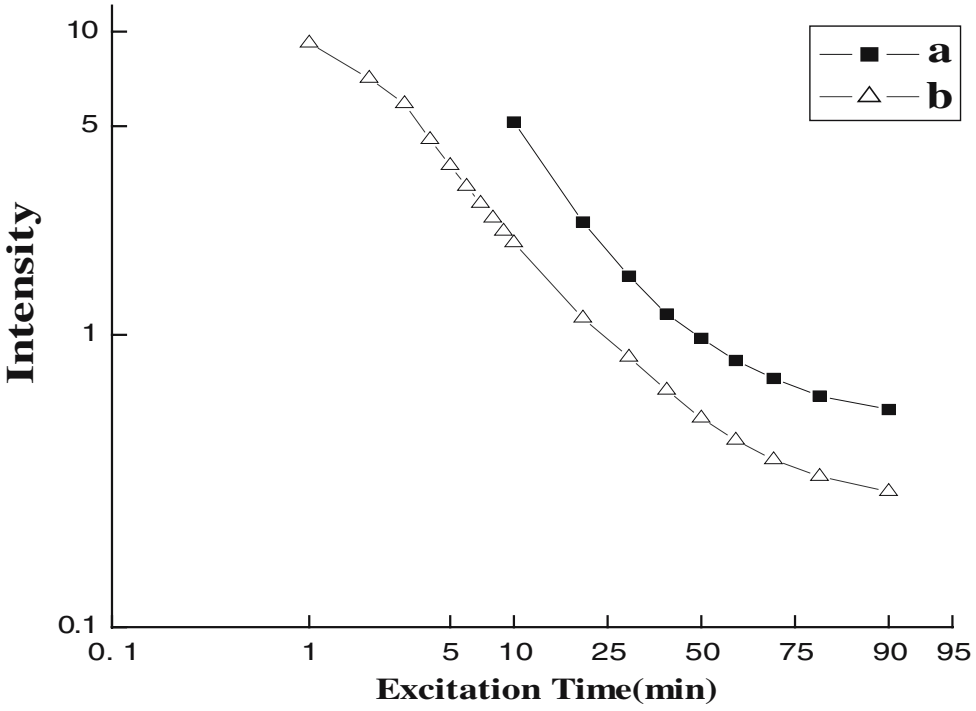

Fig. 6 Luminescent decay curves of unmodified luminescent materials: **a** unsoaked and **b** soaked in de-ionized water for a time

a time. To confirm the improvement of resistance-to-water property of the PMMA/rare earth composite luminescent materials, the luminescent decay curves of the unmodified luminescent materials and of the PMMA/rare earth composite luminescent materials were measured, respectively. Through the luminescent decay curves in Figs. 6 and 7, the performance of photoluminescence of the unmodified luminescent materials and that of the PMMA/rare earth

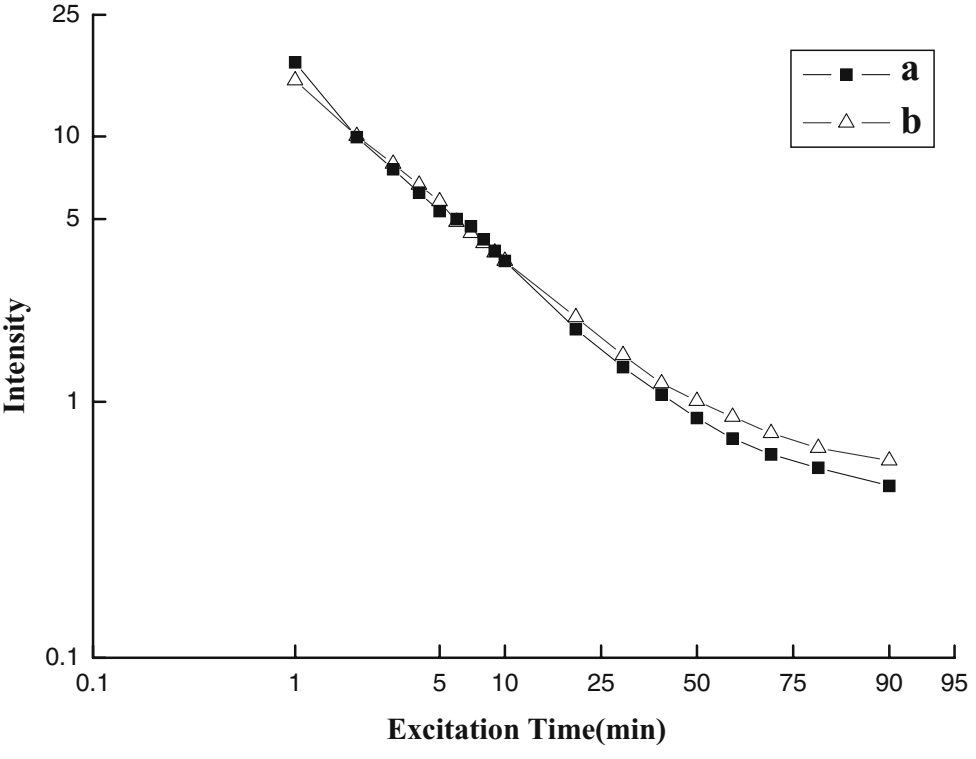

Fig. 7 Luminescent decay curve of extracted PMMA/rare earth composite luminescent materials after exciting: **a** unsoaked and **b** soaked in deionized water for a time

composite luminescent materials are studied. We find that, after the unmodified luminescent materials are soaked in distilled water, the luminance fall down. The longer the soaking time, the more the losing of luminance. On the contrary, because of forming water-resistant polymer on the surface of rare earth composite luminescent materials, the PMMA/rare earth composite luminescent materials have good stability in water. Compared with that in Fig. 6, the luminance of the PMMA/rare earth composite luminescent materials has no variation after soaking in distilled water (Fig. 7). The resistance-to-water property of the PMMA/rare earth composite luminescent materials has an obvious improvement.

Conclusion

Through modification of the luminescent materials with coupling agent and in situ emulsion polymerization of MMA in the presence of the modified luminescent materials, the PMMA/rare earth composite luminescent materials with strong interactions between the polymer and the rare earth luminescent materials can be obtained. The composite luminescent materials have excellent luminescent properties and resistance to water.

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