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ScienceDirect
Composites Science and Technology 67 (2007) 2199–2207
COMPOSITES SCIENCE AND TECHNOLOGY
www.elsevier.com/locate/compscitech

Preparation and luminescence properties of $Sm(TTA)_3phen$/NBR composites

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Received 14 September 2004; received in revised form 6 June 2005; accepted 1 July 2005

Abstract

In the present study, we examined the luminescent properties of uncured and cured samarium tris-(2-thenoyltrifluoroacetone)-1,10-phenanthroline/nitrile rubber composites ($Sm(TTA)_3phen$/NBR, i.e. Sm-complex/NBR). The formula of Sm-complex was determined by infrared spectroscopy (IR) and elementary analysis. The composites were investigated and characterized by photoluminescent (PL) spectroscopy, scanning electron microscopy (SEM) and X-rays diffraction (XRD). The characteristic emission fluorescent intensities of the Sm^{3+} in both uncured and cured composites increase with the increase of Sm-complex content. For the nitrile rubber composites with the same content of $Sm(TTA)_3phen$, the uncured composites are found to have lower luminescent intensity than that of cured composites. To explain this result, we propose that the cross-linking network structure can help to stabilize the coordination environment of the Sm^{3+} ion and improve the energy transfer efficiency from the outside energy to the central Sm^{3+} ion. In our study, the rare earth organic complexes were dispersed homogeneously into the NBR matrix. The fluorescent intensity of the composites was high and no fluorescent quenching had been observed until the complexes concentration was up to 14.3%.

Keywords: Polymer-matrix composites; Fluorescence; Nitrile rubber; Samarium; Curing

1. Introduction

Nowadays, people have great interest in rare earth organic β-diketone complexes due to their unique fluorescence properties and promising applications such as fluorescence probes [1], laser materials [2,3], especially as electroluminescence materials for potential application in large-area displays [4,5]. In the complexes, the ligands, such as β-diketones, can absorb energy from the outside environment and transfer it to the central rare earth ions (Sm(III), Eu(III) or Tb(III)). And the increase of the absorptivity of the ligand may improve the luminescent intensity of the complex. In these complexes, the [RE(-$TTA)_3$phen] complexes (RE^{3+} = Sm and Eu) have attracted a lot of attentions because of their high fluorescence emission efficiency as the result of the high absorption coefficient of the β-diketone ligand (TTA) and the synergistic effect of 1,10-phenanthroline(phen) [6–9].

In recent years, some researches on the $Sm(TTA)_3$-phen LB films have been carried out [10–12]. Although the fluorescence intensities of the $Sm(TTA)_3phen$ LB films is relatively high, it is still lower than that of the pure $Sm(TTA)_3phen$ complex. Furthermore, the complicated process to prepare this kind of luminescence materials makes their commercial production difficult.

The rare earth luminescent materials, which have polymer as the matrix, possess low-cost processing

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0266-3538/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.compscitech.2005.07.001

ability, good chemical stability and mechanical strength due to polymer nature. Compared with polymer matrix rare-earth ions composites [13–16], the polymer matrix rare-earth organic complex composites are easier to be processed [17–22]. As early as 1963, Wolff and Pressley [23] studied the laser and luminescent properties of mixed systems of $Eu(TTA)_3(H_2O)_2$/PMMA. They found that the material was like a solid solution before the material showed fluorescent quenching when the rare earth content was low. In a polymeric system developed by Ueba et al, europium was directly bonded to the PMMA. [6,24] Although the material was in a homogenous glassy phase with no grain boundaries to scatter the light, it was found that the fluorescence intensity of these Eu-coordination compounds was much weaker than that of the corresponding monomer with the same Eu^{3+} contents were the same. These researches indicated that the lower coordination number material with the rare earth β-diketone complex was, the weaker the fluorescence intensity was. Li et al. [25] chose SiO_2/(VTMOS + PMMA) as the matrix (ormosil) and successfully prepared the $Eu(TTA)_3$phen/ormosil composite phosphors by the conventional sol–gel method, and they found that the composite phosphors possessed good luminescence properties. The hybrid matrix causes a great effect on the luminescence properties of the europium complex, i.e. spectral lines were broadened and the number of lines decreased. However, the fluorescence intensities of the above composites were relatively low.

Compared with Eu, the Sm-complex/polymer matrix composites have been less studied. In this article, we synthesized the $Sm(TTA)_3$phen complex, and we chose nitrile rubber (NBR) as the matrix to prepare $Sm(TTA)_3$-phen/NBR composites with different loadings of $Sm(TTA)_3$phen complex and a small amount of peroxide in that NBR has much stronger polarity to coordinate with the rare-earth complex to some extent, and good softness to shape in preparation of optical apparatus. Because of the degradation of peroxide during cuing process, the degraded radicals of peroxide not only change the molecular structure of NBR matrix by curing it, but also affect the interaction between the Eu-complex and matrix to cause the differences in structure and property between the cured and uncured $Sm(TTA)_3$phen/NBR composites The morphology and fluorescent property of the cured and uncured composites were investigated in detail.

2. Experimental

2.1. Materials and measurements

2.1.1. Reagents and samples

Samarium oxide (Sm_2O_3, 99.99%) was purchased from Shanghai Yue Long Chemical Factory, Nitrile rubber (NBR, 41 wt%CN, $Mw \sim 50 \times 10^4 g\,mol^{-1}$) was purchased from Bayer Co., and Aldrich Chem. Co., and TTA, Phen, dicumyl peroxide (DCP), acetone and absolute ethanol were purchased from Beijing Yili Fine Chemical Limited Corporation. Other analytical grade chemicals were used without purification. $Sm(TTA)_3$-phen (shown in Fig. 1.) was synthesized according to the literature methods [26], and dried in a vacuum oven. The final products were all white powders.

2.1.2. Sample preparation and characterization

The cured or uncured $Sm(TTA)_3$phen/NBR composites comprising 2.4 wt% $Sm(TTA)_3$phen in NBR was prepared by mixing 100 g of the NBR, 3 g of the DCP and 2.7 g of the Sm-complex in a clean mixer (Haake, rheomix610,Ger.) at 50 °C and at 80 rpm for 15 min. Then, the achieved compound was put into the window mould of 1-mm thickness and vulcanized under the pressure of 15 MPa for 20 min at 160 °C to obtain the cured composites, while the uncured composites was prepared under pressure of 15 MPa for 20 min at 80 °C (under this condition the curing agent DCP does not react). Other cured and uncured composites with different percentages of $Sm(TTA)_3$phen complex (2.4, 4.7, 7.0, 9.1 and 14.3 wt%, respectively) were prepared according to the same procedure.

The infrared spectra of the synthesized pure $Sm(TTA)_3$phen complex were measured by a Toshiba 270–30 Fourier Infrared Spectroscope with KBr pellet technique. The X-ray diffraction of composites was performed by a D/max2500 diffractometer (Cu LFF, 40 kV and 20 mA, $\lambda = 0.154$ nm). Samples of 1-mm (thick) × 2-mm (wide) × 10-mm (long specimens) were cut and applied for XRD investigation. The photoluminescent spectra of the samples were recorded by a Hitachi F-4500. Fluorescent spectrometer was equipped with a 450-W Xenon lamp as the excitation source with excitation and emission slit width of 2.5 nm. Samples of 1 × 1 cm cut from the 1.0-mm thick sheet of the cured or uncured Sm-complex/NBR composites were used for the fluorescence measurement. Morphologies of composites were observed by using scanning electron micrographs (SEM; Cambridge S-250-III, LaB_6, 20-kV, vacuum level was 10^{-5} Pa). The fracture surfaces of composites were obtained by breaking the long strip samples in liquid nitrogen, and each sample was covered by gold vapor under vacuum for SEM observation. All tests were carried out at room temperature.

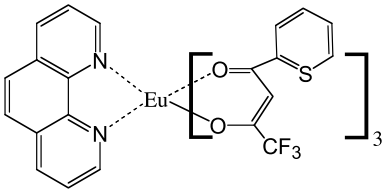

Fig. 1. Molecular structure of $Sm(TTA)_3$phen.