

# Preparation of Tb(Pht)<sub>3</sub>Phen/Rubber Composites and Characterization of Their Fluorescent Properties

Cheng Yang,<sup>1</sup> Li Liu,<sup>1</sup> Yonglai Lu,<sup>2</sup> Lei He,<sup>2</sup> Wan Zhang,<sup>2</sup> Liqun Zhang<sup>1,2</sup>

<sup>1</sup>Key Laboratory of Beijing City on the Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

<sup>2</sup>Key Laboratory for Nanomaterials of the Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

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**ABSTRACT:** A rare-earth ternary complex compound, Tris-(terbium-phthalate)-1, 10-phenanthroline Terbium (III) [Tb(Pht)<sub>3</sub>Phen], was synthesized through the reaction among a rare-earth oxide (Tb<sub>4</sub>O<sub>7</sub>), potassium hydrogen phthalate and phenanthroline, and its structure was characterized with scanning electron microscopy (SEM), laser particle size (LPS), IR, and X-ray diffraction. This was the first time that Tb(Pht)<sub>3</sub>Phen/rubber [nitrile butadiene rubber (NBR) or methyl vinyl silicone rubber (SiR)] composites had been prepared through mechanical mixing processing. SEM revealed that the dimensions of Tb(Pht)<sub>3</sub>Phen dispersed in matrix rubber were much smaller than those of the original particles of the complex compound. The Tb(Pht)<sub>3</sub>Phen/rub-

ber composites showed much better luminescent performance than the Tb(Pht)<sub>3</sub>Phen complex compound. The fluorescent intensities of the Tb(Pht)<sub>3</sub>Phen/rubber composites were strongly dependant on the concentration of Tb(Pht)<sub>3</sub>Phen, and 30 phr was the optimal concentration for both the Tb(Pht)<sub>3</sub>Phen/NBR and Tb(Pht)<sub>3</sub>Phen/SiR composites. Within the concentration range of Tb(Pht)<sub>3</sub>Phen used in this work, the fluorescent intensions of the SiR composites were stronger than those of their NBR counterparts. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 20–28, 2005

**Key words:** composites; fluorescence; rubber

## INTRODUCTION

The triplet-excited states of most aromatic acid ligands, such as potassium hydrogen phthalate (KHPht), match the resonant emission states of Tb<sup>3+</sup> ions well. Their complex compounds can produce the strong characteristic emissions of the rare-earth ions, and they exhibit excellent luminescent properties.<sup>1–4</sup> Similar to rare-earth-biology complex compounds, they are prepared through the coordination of carboxyl and rare-earth ions. Therefore, the study of this kind of complex compound will improve our understanding of the structure and function of rare-earth-biology complex compounds.<sup>5–7</sup> The main radiation (<sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub>) of Tb<sup>3+</sup> is so close to the range of human

eyesight that it is a luminescent substance with substantial value.<sup>8</sup> Some researchers<sup>9–12</sup> have previously shown that composites prepared by the mixing of aromatic acid/Tb<sup>3+</sup>-ion complex compounds with polymers have some applied and theoretical values. There are three methods of preparing organic rare-earth/polymer luminescent composites. The first one is the direct distribution of rare-earth fluorescent complex compounds into polymers. For this method, solution blending is in common use. For instance, aromatic or heterocyclic acid compounds of Tb<sup>3+</sup> or Eu<sup>3+</sup> and soluble polymers were dissolved in a solvent at the same time, and the solution was heated to remove the solvent and form rare-earth/polymer composites, or the fine powders of a rare-earth complex compound were uniformly mixed in a polymer solution and then, through some specific processing, rare-earth/polymer composites were produced.<sup>13</sup> The second method is the mixing of a rare earth (Tb<sup>3+</sup> or Eu<sup>3+</sup>) with a polymer whose chains contain organic ligands, such as dibenzoglmethane, benzoylacetone, and thenoyltrifluoroacetone (TTA); this forms rare-earth/polymer composites through their coordination reaction.<sup>14</sup> The last method involves the synthesis of some organic complex compounds first, which can take part in an epichlorohydrin reaction, and then their polymeriza-

Correspondence to: L. Zhang (zhangliqunghp@yahoo.com)

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TABLE I  
Raw Materials and Reagents

Material or reagent	Abbreviation	Grade or trademark	Manufacturer
Tb <sub>4</sub> O <sub>7</sub>		99.99%	Shanghai Yuelong Non-Ferrous Metals Co., Ltd. (Shanghai City, China)
Potassium hydrogen phthalate (KHC <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )	KHPht	Analytical reagent	Beijing Yili Fine Chemicals Co., Ltd. (Beijing, China)
Phenanthroline	Phen	Analytical reagent	Beijing Xizhong Chemical Factory (Beijing, China)
Thenoyltrifluoroacetone (C <sub>8</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> S)	TTA	99%	J&K China Chemical Ltd. (Beijing, China)
Ammonia water		Analytical reagent	Beijing Chemical Factory (Beijing, China)
Anhydrous alcohol		Analytical reagent	Beijing Chemical Factory (Beijing, China)
Hydrochloric acid (HCl)		36–38%	Commercial product
Nitrile butadiene rubber	NBR	NBR41	Lanzhou Chemical Industry Co. (Gansu Province, China)
Methyl vinyl silicone rubber	SiR	110–2	Beijing Chemical No. 2 Factory (Beijing, China)
Dicumyl peroxide	DCP	Chemical Purity	Shanghai Jinlong Chemical Reagents Co., Ltd. (Shanghai City, China)
2,5-Dimethyl 2,5-bis( <i>t</i> -butyl peroxy) hexyne	D25	85%	Beijing Chemical Reagents Co. (Beijing, China)

tion with organic monomers to obtain macromolecular complex compounds with high luminescent efficiency.<sup>15</sup> In this work, we used mechanical blending and stationary vulcanization to prepare Tb(Pht)<sub>3</sub>-Phen/rubber composites that had high luminescent properties, were low-cost, and involved only a simple technique.

## EXPERIMENTAL

### Raw materials and reagents

The raw materials and reagents used in this work and their manufacturers are listed in Table I.

### Preparation of the Tb(Pht)<sub>3</sub>Phen complex compound

The Tb(Pht)<sub>3</sub>Phen complex compound was prepared through the mixing of Tb<sub>4</sub>O<sub>7</sub>, phenanthroline (Phen), and KHPht in a molar ratio of 0.25:1:3. In this work, 0.0125 mol of Tb<sub>4</sub>O<sub>7</sub>, 30 mL of HCl, and 30 mL of H<sub>2</sub>O were milled at 80–90°C. After about 3 h, the solution became transparent. At that time, continued heating was required to get rid of the extra HCl. Then, 0.15 mol of KHPht, 30 mL of ethanol, and 30 mL of H<sub>2</sub>O were mixed with the solution for 1 h. Finally, 0.05 mol of Phen, 30 mL of ethanol, and 30 mL of H<sub>2</sub>O were mixed with the solution for 8 h to form a transparent solution. Then, the reaction mixture was cooled to room temperature. Ammonia water (1:1) was added to the solution to adjust the pH of the solution to 6–7 for precipitation. The precipitate was filtered *in vacuo* and washed several times until a white complex com-

pound was separated out. The compound was first dried with a blower at 80°C and then dried *in vacuo* until the weight remained constant. The Tb(Pht)<sub>3</sub>Phen complex compound prepared by this method was a white powder.

### Preparation of the Tb(Pht)<sub>3</sub>Phen/rubber composites

The rubber compounds (i.e., uncured composites), containing 100 parts (by weight) nitrile butadiene rubber (NBR) or methyl vinyl silicone rubber (SiR), 3 phr 2,5-methyl 2,5-bis(*t*-butyl peroxy)hexyne (D25) for NBR or 5 phr dicumyl peroxide (DCP) for SiR, and various amounts of the Tb(Pht)<sub>3</sub>Phen complex compound (5, 10, 20, 30, or 40 phr), were masticated on a two-roll mill (Φ152.4) at room temperature. Specimens of the cured Tb(Pht)<sub>3</sub>Phen/rubber composites (10 mm × 15 mm × 2 mm) were molded at 170°C for appropriate times.

### Measurements

Scanning electron microscopy (SEM) observations of the powder of the Tb(Pht)<sub>3</sub>Phen complex compound and Tb(Pht)<sub>3</sub>Phen/rubber composites were made on an S-250-III scanning electron microscope (Cambridge Co., UK). The granularity distribution of the Tb(Pht)<sub>3</sub>Phen powder was examined with a Mastersizer 2000 (Malvern Co., UK) laser granularity instrument, and alcohol was used as the dispersion medium. The IR spectrum of Tb(Pht)<sub>3</sub>Phen was recorded at a resolution of 4 cm<sup>-1</sup> on a Hitachi 270-30 Fourier transform infrared (FTIR) spectrometer (Hitachi Co., Ja-

pan). The UV spectra of pristine NBR and SiR were measured with a Cintra20 UV spectrometer (GBC Co., Dandenong, Australia). Wide-angle X-ray diffraction (WAXD) experiments of the complex compound and its rubber composites were carried out on a D/MAX2500+PC X-ray diffractometer (REGAKU Co., Japan) with Cu  $K\alpha$  radiation ( $\lambda \sim 1.54 \text{ \AA}$ ). The fluorescent properties were examined on a Hitachi F-4500 fluorescence spectrometer at a scanning rate of 2400 nm/min and a scanning voltage of 400 V. The width of the scanning slit was 5.0 nm/5.0 nm (excitation/emission).

## RESULTS AND DISCUSSION

### SEM morphologies of the complex compound and its rubber composites

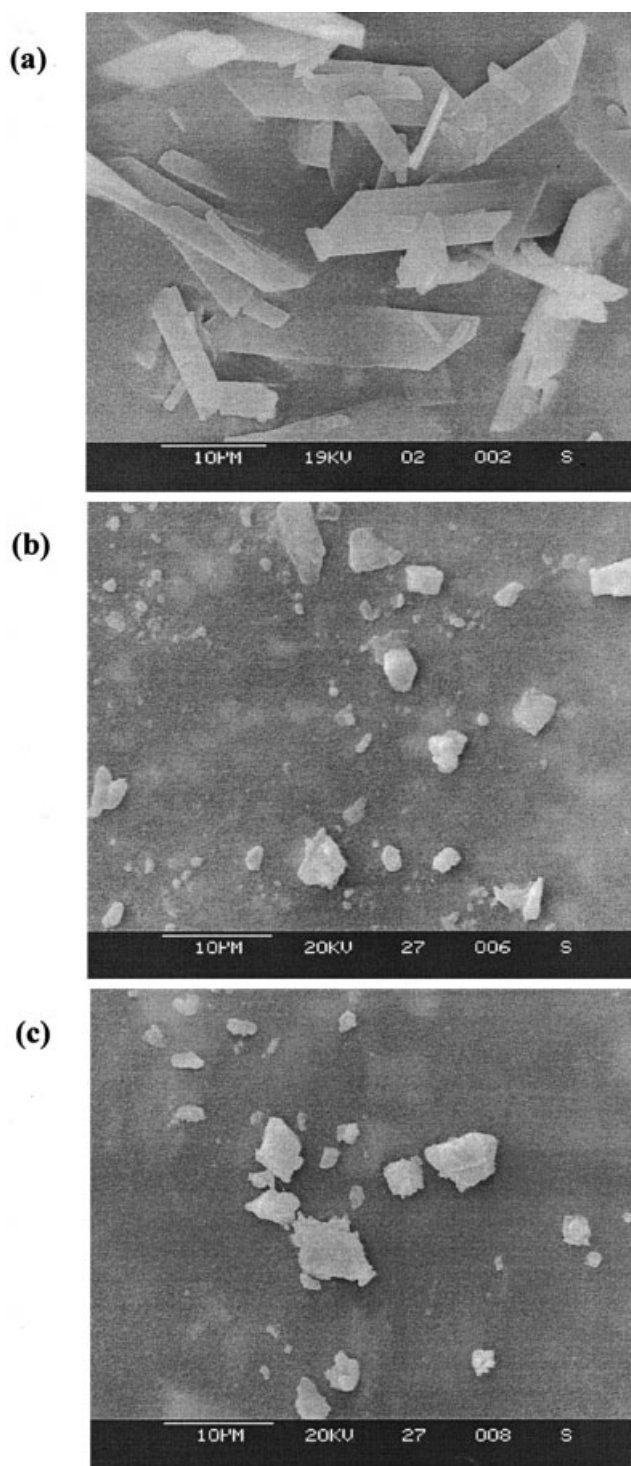
SEM photographs of the  $\text{Tb}(\text{Pht})_3\text{Phen}$  and  $\text{Tb}(\text{Pht})_3\text{Phen}$ /rubber composites are shown in Figure 1. Figure 1(a) shows that the original particles of  $\text{Tb}(\text{Pht})_3\text{Phen}$  are regularly shaped, suggesting that it is a crystal substance, and its smallest size is about  $2 \mu\text{m}$ . Figure 1(b,c) demonstrates that the dimensions of the  $\text{Tb}(\text{Pht})_3\text{Phen}$  particles in the  $\text{Tb}(\text{Pht})_3\text{Phen}$ /rubber composites decrease remarkably in comparison with their original size because of strong shear stress during the mechanical mixing of  $\text{Tb}(\text{Pht})_3\text{Phen}$  with the rubbers. Moreover, the shape of the particles changes from a regular bar to an irregular granule. All these factors facilitate the interface combination between  $\text{Tb}(\text{Pht})_3\text{Phen}$  and the rubber matrix, the formation of a possible environment of coordination between the complex compound and rubbers, and the reduction of the loss of energy caused by non-radiation transition, which finally results in an enhancement of the illuminant efficiency.

### Laser granularity

The laser granularity analyses of the original  $\text{Tb}(\text{Pht})_3\text{Phen}$  particles, as shown in Figure 2, indicate that the dimension distribution of the  $\text{Tb}(\text{Pht})_3\text{Phen}$  original particle is relatively narrow. The diameters of  $d(0.1)$ ,  $d(0.5)$ , and  $d(0.9)$  are 1.905, 2.791, and  $5.091 \mu\text{m}$ , respectively, and this means that the diameters of half of the particles are less than  $2.791 \mu\text{m}$ .

### IR spectrum of $\text{Tb}(\text{Pht})_3\text{Phen}$

The IR spectrum of  $\text{Tb}(\text{Pht})_3\text{Phen}$  is shown in Figure 3. There are three IR characteristic bands associated with the carboxyl group of KHPht:  $\nu(\text{O—H})$  from  $3700$  to  $3200 \text{ cm}^{-1}$ ,  $\nu(\text{C=O})$  at  $1705 \text{ cm}^{-1}$ , and  $\delta(\text{O—H})$  at  $952 \text{ cm}^{-1}$ . In the IR spectrum of  $\text{Tb}(\text{Pht})_3\text{Phen}$ , the latter two bands disappear, but new bands at  $1547$  and  $1421 \text{ cm}^{-1}$ , overlapping the absorption of  $\delta(\text{C—H})$ , appear, which are



**Figure 1** SEM morphologies of (a) the  $\text{Tb}(\text{Pht})_3\text{Phen}$  complex compound, (b) its NBR composites, and (c) its SiR composites.

assigned to  $\nu_{as}(\text{COO}^-)$  and  $\nu_s(\text{COO}^-)$ . This result proves that a coordination reaction between  $\text{Tb}_4\text{O}_7$  and KHPht takes place and that  $\text{COO}^-$  groups generate. The existence of a  $\nu(\text{O—H})$  band might be attributed to unreacted KHPht and residual water in the complex compound.

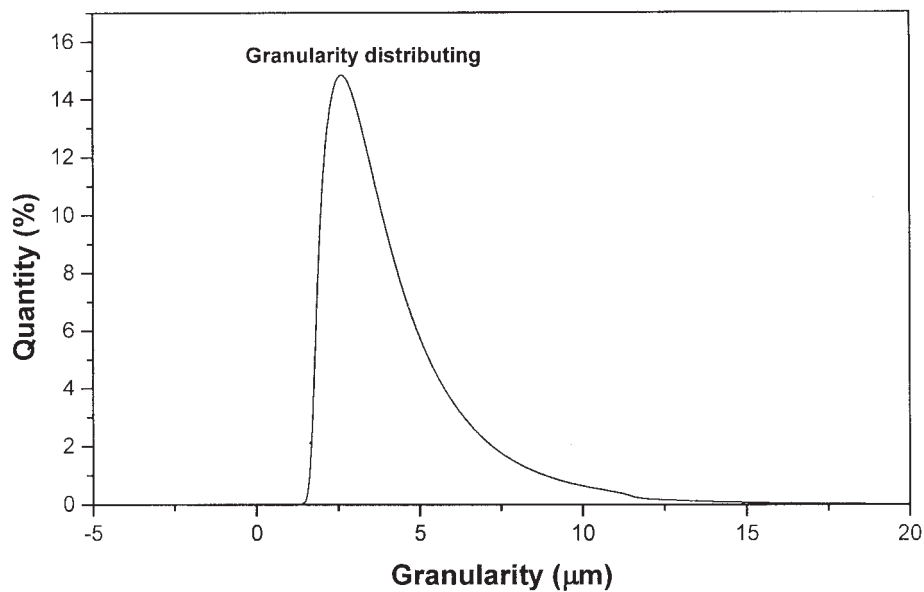


Figure 2 Laser granularity distribution analysis of the original Tb(Pht)<sub>3</sub>Phen particles.

#### WAXD patterns of the complex compound and its rubber composites

In the WAXD pattern of the Tb(Pht)<sub>3</sub>Phen powder shown in Figure 4, there are some extremely strong reflection crystalline signals at  $2\theta$  angles of 7.48, 22.64, 38.22, and 39.56°, and amorphous scattering is absent. This reveals that Tb(Pht)<sub>3</sub>Phen is a crystal substance with a highly perfect lattice structure. Figure 5 depicts WAXD patterns of Tb(Pht)<sub>3</sub>Phen/NBR and Tb(Pht)<sub>3</sub>Phen/SiR. In these patterns, the strong characteristic reflections for

crystalline Tb(Pht)<sub>3</sub>Phen still exist, and this shows that the crystalline structure of Tb(Pht)<sub>3</sub>Phen in the rubber composites changes little. However, the breadth of the reflection peaks becomes broader than the breadth of those of the original Tb(Pht)<sub>3</sub>Phen powder, and this means that the crystalline dimensions of Tb(Pht)<sub>3</sub>Phen in the rubber composites are smaller than those of the original Tb(Pht)<sub>3</sub>Phen particles. For example, the width at the half-intensity of the reflection at 7.48° for the original Tb(Pht)<sub>3</sub>Phen powder is 0.122°, whereas those

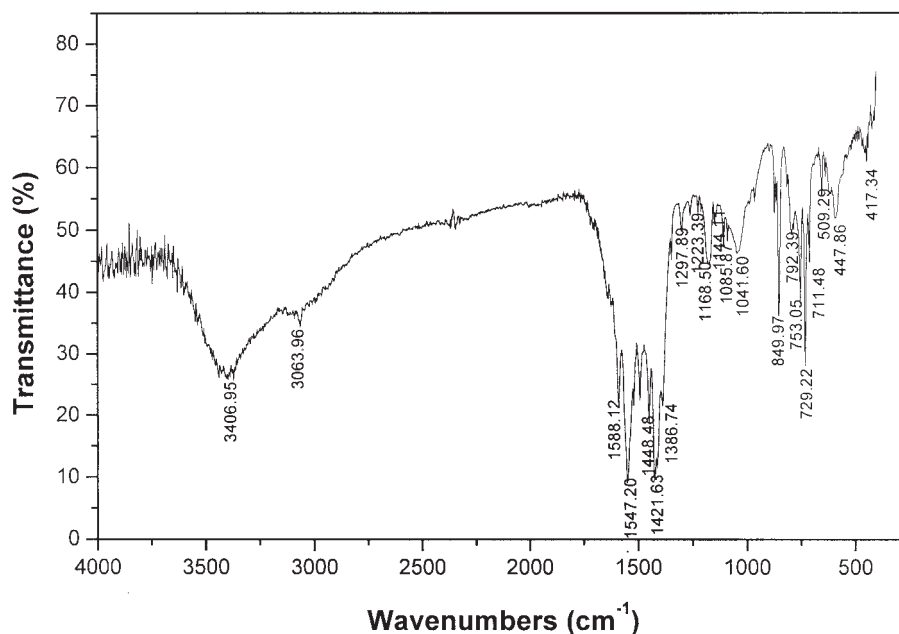


Figure 3 FTIR spectrum of Tb(Pht)<sub>3</sub>Phen.

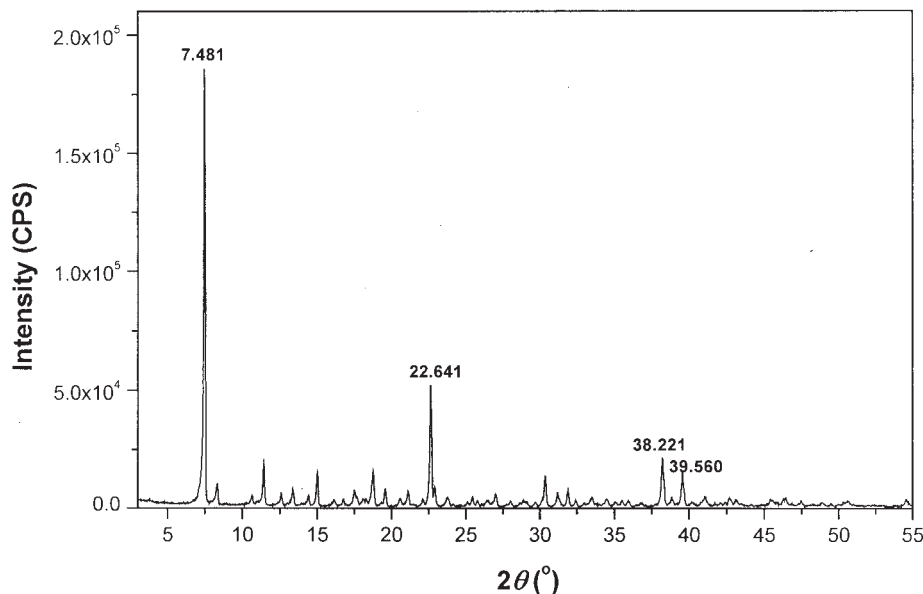


Figure 4 WAXD pattern of the  $\text{Tb(Pht)}_3\text{Phen}$  powder.

for  $\text{Tb(Pht)}_3\text{Phen/NBR}$  and  $\text{Tb(Pht)}_3\text{Phen/SiR}$  are  $0.14$  and  $0.173^\circ$ , respectively. These WAXD results agree with the SEM observations. The amorphous scattering in the WAXD patterns of the composites is likely associated with the matrix rubbers in the amorphous state.

#### Fluorescent properties of the complex compound and its rubber composites

Figures 6(a) and 7(a) display the excitation spectra of  $\text{Tb(Pht)}_3\text{Phen}$  and its rubber composites, from which the optimal excitation wavelength (310 nm) for mea-

suring their emission spectra has been determined. The emission spectra of the complex compound and its rubber composites [Figs. 6(b) and 7(b)] demonstrate that the fluorescent intensity of the  $\text{Tb(Pht)}_3\text{Phen/}$  rubber composites is strongly dependant on the loading of the complex compound. The main radiation band is at 545.2 nm and is assigned to  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ . In Figure 7(b), the fluorescent intensity of  $\text{Tb(Pht)}_3\text{Phen/SiR}$  (30/100) at this radiation is so strong that it exceeds the test limits of the instrument, and so the exact fluorescent intensity of  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  for these composites

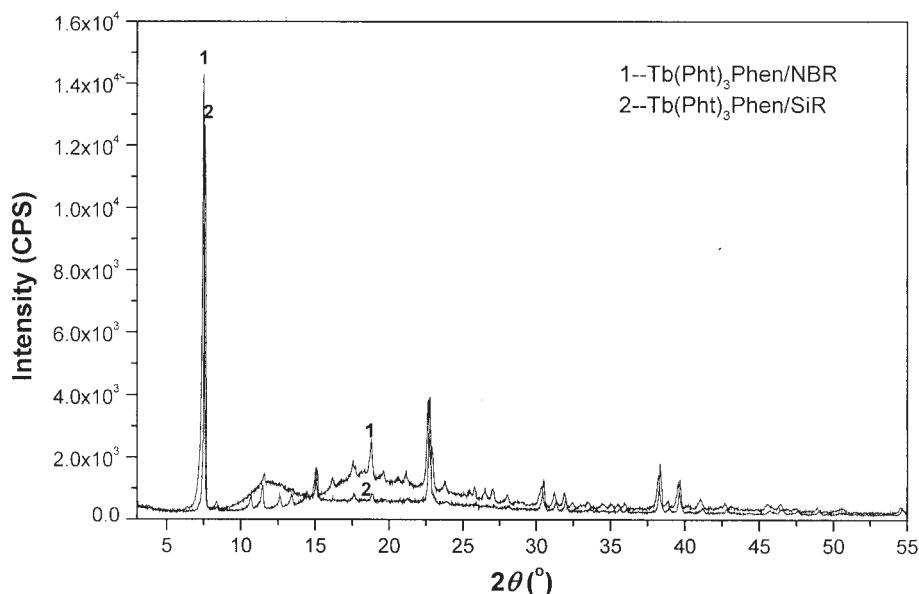
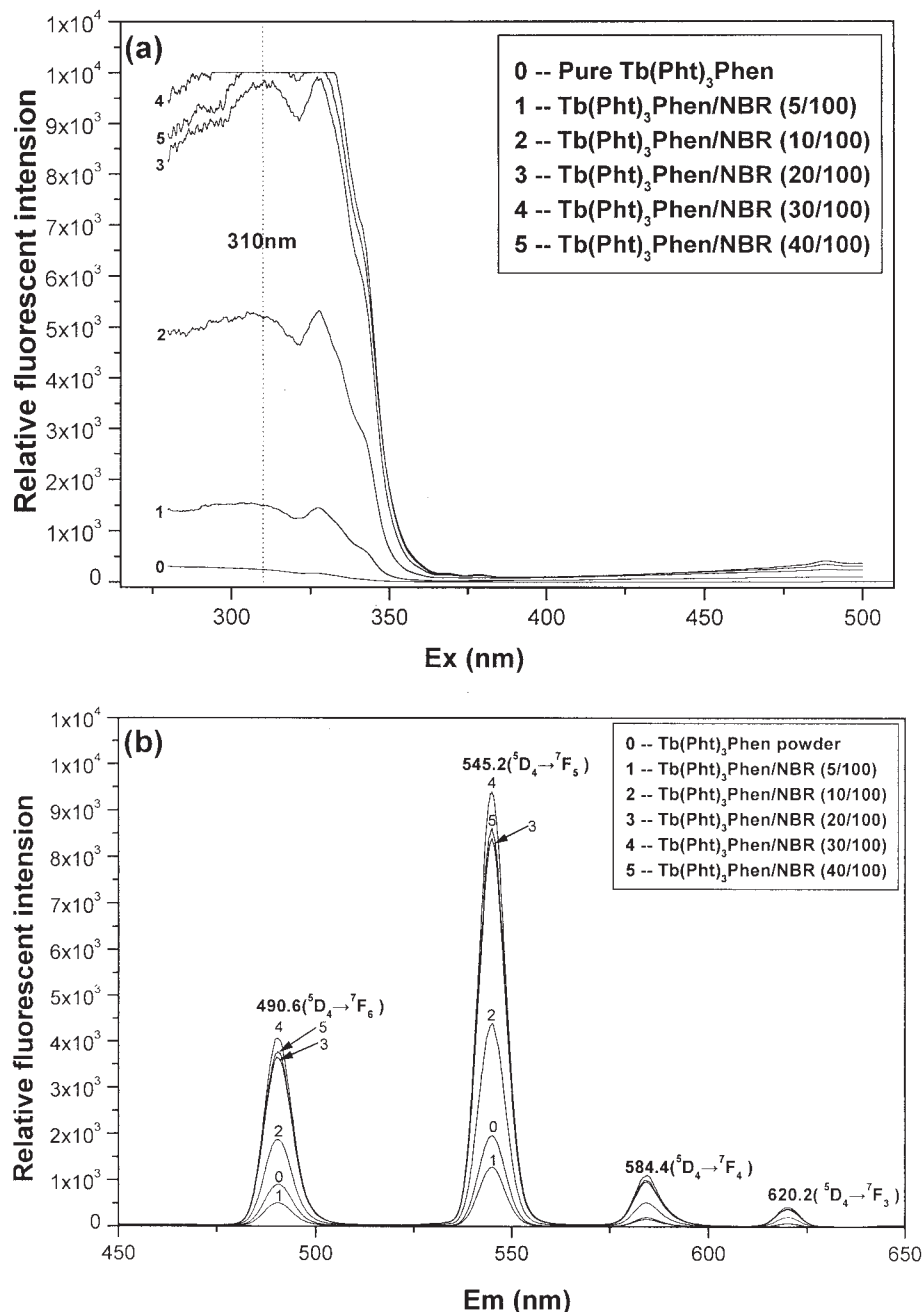


Figure 5 WAXD patterns of the  $\text{Tb(Pht)}_3\text{Phen/NBR}$  and  $\text{Tb(Pht)}_3\text{Phen/SiR}$  composites.

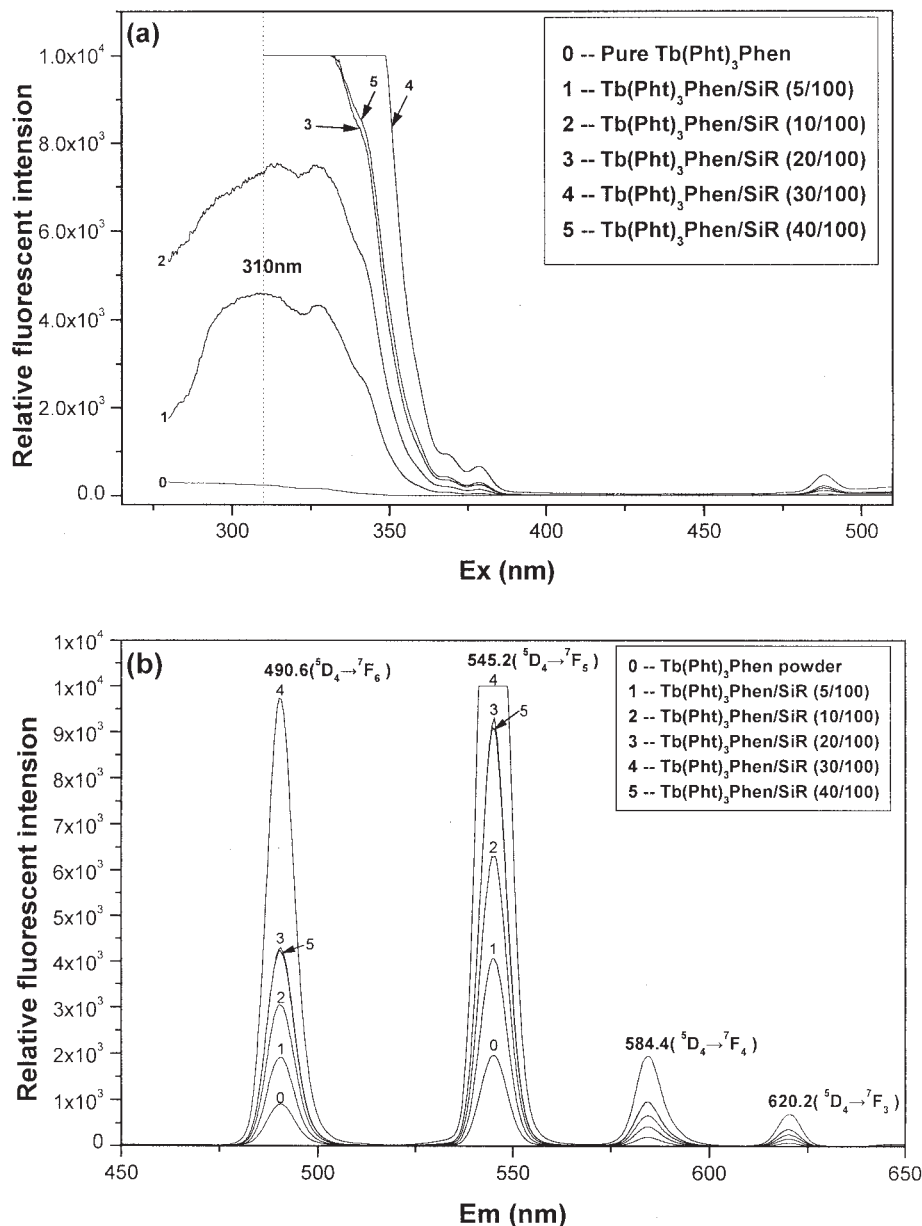




**Figure 6** (a) Excitation (Ex) and (b) emission (Em) spectra of Tb(Pht)<sub>3</sub>Phen and its NBR composites (excitation = 310 nm).

cannot be obtained. However, the intensity of the second strong radiation band at 490.6 nm is within the test limit and might be correlated to that of the main radiation one. Figure 8 reveals that there is a linear relationship between the fluorescent intensities of these two radiations. According to this relationship, the fluorescent intensity of <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> radiation for Tb(Pht)<sub>3</sub>Phen/SiR (30/100) can be estimated from that of the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>6</sub> one, and the resultant value is 22,396. Consequently, the radiation at 490.6 nm has been selected to discuss the influence of the Tb(Pht)<sub>3</sub>Phen

loading on the fluorescent intensities of the composites, and the results should be the same as those derived from the main radiation. Figure 9 shows that the fluorescent intensities at 490.6 nm of both Tb(Pht)<sub>3</sub>Phen/NBR and Tb(Pht)<sub>3</sub>Phen/SiR increase with the loading of Tb(Pht)<sub>3</sub>Phen and then drop after reaching the maximal values at the loading of 30 phr. Within the loading range of the complex compound involved in this work, the fluorescent intensities of the SiR composites are always larger than those of their NBR counterparts and also higher than that of pure



**Figure 7** (a) Excitation (Ex) and (b) emission (Em) spectra of Tb(Pht)<sub>3</sub>Phen and its SiR composites (excitation = 310 nm).

Tb(Pht)<sub>3</sub>Phen. The fluorescent intensity of the NBR composites is not stronger than that of the complex compound until the loading of Tb(Pht)<sub>3</sub>Phen is greater than 6.5 phr. It is very interesting and important that the changing degree of the fluorescent intensity for the SiR composites is much greater than that for the NBR composites in the loading range of 20–40 phr. The strongest fluorescent intensities of the NBR and SiR composites are 4.5 and 10.7 times, respectively, as high as that of the pure complex compound; they are also higher than those of other reported polymer composites based on Tb.<sup>1,8,16</sup>

When the Tb(Pht)<sub>3</sub>Phen powder assembles together, the contacting surface transfers energy, and this re-

sults in fluorescent quenching and an extreme reduction in the luminescent intensity. When the powder of the Tb complex compound is dispersed in the rubber, the fluorescent quenching caused by the aggregation of the Tb(Pht)<sub>3</sub>Phen powder is restrained by the separation effect of the polymer matrix, and this leads to increased luminescent efficiency. When the concentration of Tb(Pht)<sub>3</sub>Phen is beyond a certain level, some Tb(Pht)<sub>3</sub>Phen particles in the composite become aggregate, and fluorescent quenching occurs. In this work, the laser source used for the measurements of the emission spectra was UV light at a wavelength of 310 nm. The UV spectra of pure NBR and SiR were recorded, and the results are shown in Figure 10. The

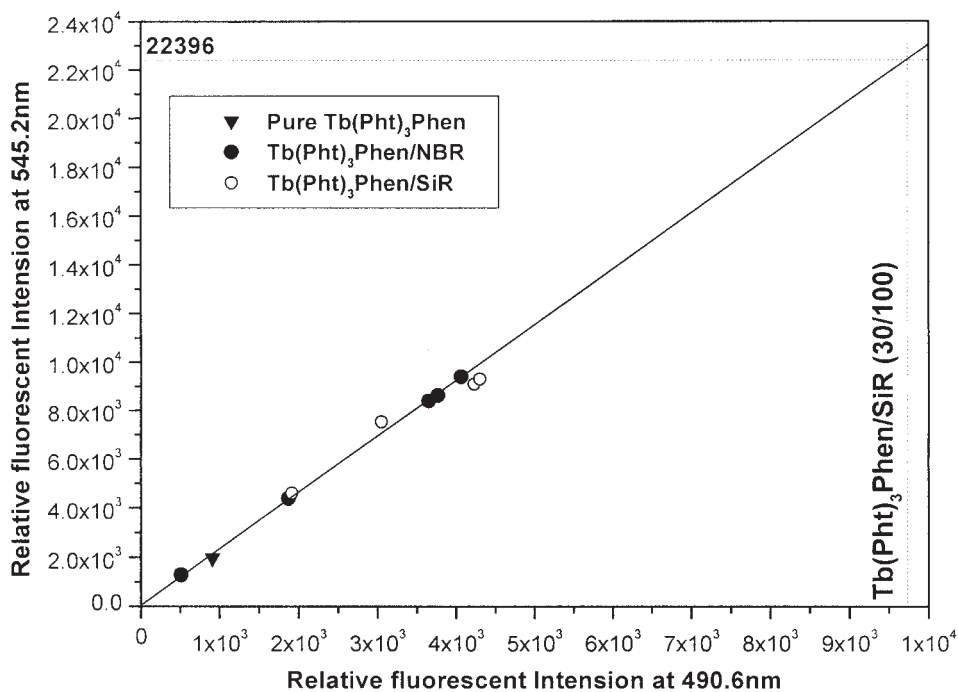


Figure 8 Relationship between the relative fluorescent intensities at 490.6 and 545.2 nm.

strong absorption range of UV for NBR is within 180–320 nm, whereas that for SiR is within 180–250 nm. As a result, in the Tb(Pht)<sub>3</sub>Phen/NBR composites, most of the UV light is absorbed by the NBR matrix, and this weakens the intensity of the excitation light exerted on the dispersed Tb(Pht)<sub>3</sub>Phen complex compound. On the other hand, in the Tb(Pht)<sub>3</sub>Phen/SiR

composites, the UV light of 310 nm can almost entirely permeate through the matrix, and so dispersed Tb(Pht)<sub>3</sub>Phen can emit far stronger fluorescence, especially at a loading of 30 phr. This result implies that the fluorescent intensity of the Tb(Pht)<sub>3</sub>Phen/polymer composites can be adjusted artificially over a wide scale by the alteration of the matrix polymer with

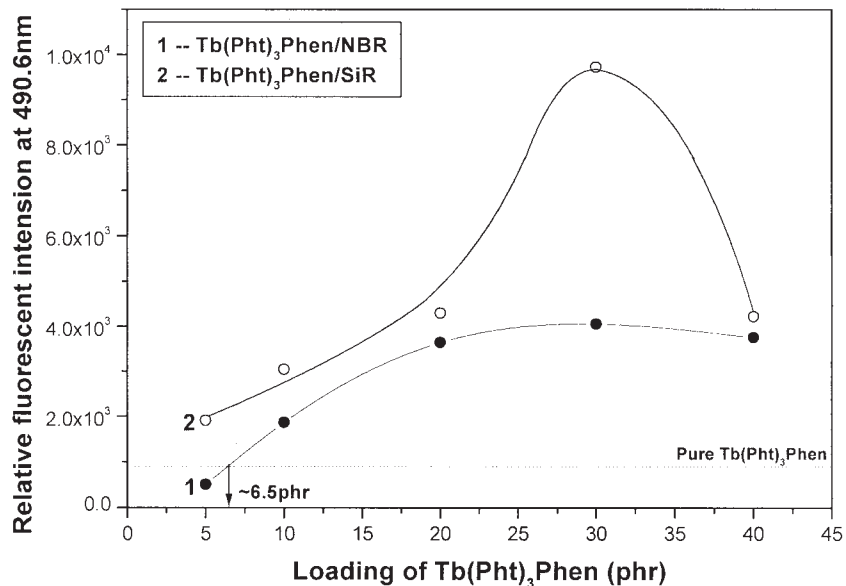


Figure 9 Dependence of the fluorescent intensities of the Tb(Pht)<sub>3</sub>Phen/NBR and Tb(Pht)<sub>3</sub>Phen/SiR composites on the loading of Tb(Pht)<sub>3</sub>Phen.



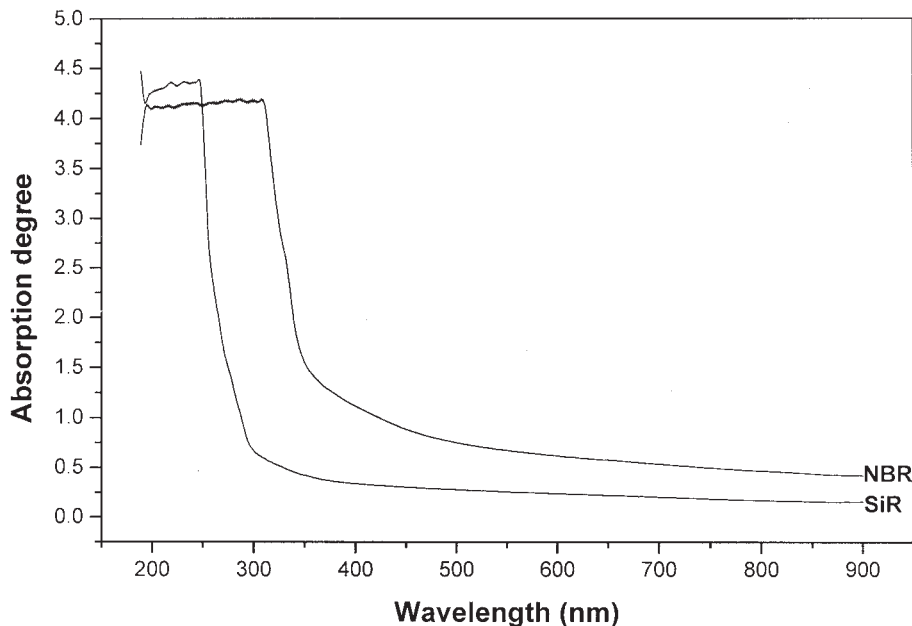


Figure 10 UV spectra of NBR and SiR.

different UV absorption features. However, the precise reason for the sudden change in the fluorescent intensity of the SiR composites within the 20–40 phr concentration range of  $\text{Tb}(\text{Pht})_3\text{Phen}$  is still unclear and requires further investigation.

### CONCLUSIONS

The fluorescent intensities of both  $\text{Tb}(\text{Pht})_3\text{Phen}/\text{NBR}$  and  $\text{Tb}(\text{Pht})_3\text{Phen}/\text{SiR}$  improve as the concentration of  $\text{Tb}(\text{Pht})_3\text{Phen}$  increases and then drop down after reaching the maximal values at the loading of 30 phr because of the appearance of fluorescence quenching.

At the same filling concentration of  $\text{Tb}(\text{Pht})_3\text{Phen}$ , the fluorescent intensities of the  $\text{Tb}(\text{Pht})_3\text{Phen}/\text{SiR}$  composites are stronger than those of  $\text{Tb}(\text{Pht})_3\text{Phen}/\text{NBR}$ . In particular, the fluorescent intensity of  $\text{Tb}(\text{Pht})_3\text{Phen}/\text{SiR}$  is unexpectedly strong in the loading range of 20–40 phr, and the strongest intensity is 10.7 times higher than that of pure  $\text{Tb}(\text{Pht})_3\text{Phen}$ .

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