

# Preparation and characterisation of luminescent composite materials based on polylactic acid

Jiang Zhu<sup>1</sup>, Jiang Cheng<sup>2</sup>, Haitao Ni<sup>1</sup> ✉, Yingying He<sup>1</sup>, Tao Tang<sup>1</sup>

<sup>1</sup>College of Materials and Chemical Engineering, Chongqing University of Arts and Sciences, Yongchuan, Chongqing 402160, People's Republic of China

<sup>2</sup>Co-Innovation Center for Micro/Nano Optoelectronic Materials and Devices, Chongqing University of Arts and Sciences, Yongchuan, Chongqing 402160, People's Republic of China

✉ E-mail: htniok@163.com

Published in Micro & Nano Letters; Received on 18th May 2018; Revised on 27th October 2018; Accepted on 13th November 2018

A ternary complex of Tb(SSA)<sub>3</sub>Phen was synthesised based on terbium(III) (Tb<sup>3+</sup>) ion and the ligands including 1,10-phenanthroline (Phen) and 5-sulfosalicylic acid (SSA). Then a series of polylactic acid (PLA)/Tb(SSA)<sub>3</sub>Phen composites were prepared by the melt-mixing process. The luminescent properties of PLA/Tb(SSA)<sub>3</sub>Phen composite films were investigated by fluorescence spectrophotometry. The spectra of all composites indicated that PLA/Tb(SSA)<sub>3</sub>Phen composites shown the characteristic bright green fluorescence which originated from Tb(SSA)<sub>3</sub>Phen. Moreover, the energy absorption and transfers of Tb(SSA)<sub>3</sub>Phen were slightly affected by the PLA matrix. The optical transmittance of the composites was measured by the UV-vis spectrometer. The results demonstrated that Tb(SSA)<sub>3</sub>Phen can ameliorate the PLA film transparence, which well dispersed in the PLA matrix. Moreover, the thermal properties, crystal structure and the mechanical properties of PLA/Tb(SSA)<sub>3</sub>Phen composite were also investigated to determine the potential usage as a green fluorescent material.

**1. Introduction:** A considerable number of research reports have focused on luminescent polymer-rare earth complexes, due to their excellent mechanical flexibility and good processibility, especially fine film-forming property [1–3]. These advantages will accelerate their applications greatly in enable expandable and foldable screens for smartphones, wearable or fashionable electronic clothing, rollable or collapsible wallpaper-like lamps and biocompatible light sources for in vivo or epidermal medical devices [4–6]. In the past few decades, polymer-rare earth complexes have achieved great progress, various luminescent polymer-rare earth complexes (polystyrene (PS), polymethyl methacrylate (PMMA) and polysulfone (PSF)) were prepared [2, 7, 8]. However, an increasing attention has been paid to the potential impact on the environmental systems because of their non-degradability. In this Letter, such polymers that are renewable and compostable have shown great promise as environmentally friendly alternatives to traditional polymer materials.

As one of the most ideal environmental friendly materials, polylactic acid (PLA) can be sustainable, biocompatible and compostable at the end of its life-cycle [9]. Interestingly, its transparency and refractive index are similar to those of PMMA. Therefore, the study about PA matrix has potential application prospects in the field of optoelectronics. However, there is still a dearth of the information about the preparation of PLA materials blending with rare earth complexes. Therefore, the aim of this Letter was focused on the preparation of poly(butylsuccinate)/polyvinyl carbazole (PBSPVK) composites for the flexible light-emitting devices. First, a ternary complex of Tb(SSA)<sub>3</sub>Phen was synthesised based on terbium(III) (Tb<sup>3+</sup>) ion and the ligands including 1,10-phenanthroline (Phen) and 5-sulfosalicylic acid (SSA). Then a series of PLA/Tb(SSA)<sub>3</sub>Phen materials were prepared by the melt-mixing process. The luminescent properties, the thermal behaviours, the crystal structures and the mechanical properties of PLA/Tb(SSA)<sub>3</sub>Phen composites were investigated to determine the potential usage as a green fluorescent material. Studies on the photovoltaic devices based on the composites are still in process and will be reported later.

## 2. Experimental

**2.1. Materials:** PLA, (Ingeo biopolymer 4032D) was obtained from NatureWorks LLC. Terbium oxide (Tb<sub>2</sub>O<sub>3</sub>) at the purity 99.99% was supplied by Shanghai Yue Long Rare Earth New materials Co., Ltd., China. Acroleic acid (AA, AR), 1,10-phenanthroline (Phen, AR), dimethyl sulfoxide (DMSO, AR), absolute ethyl alcohol (EA, AR), sodium hydroxide (NaOH, AR), acetone (AR), concentrated hydrochloric acid (HCl, AR) and SSA were all produced by Chengdu Kelong Chemical Reagent Factory, China.

**2.2. Preparation of Tb(SSA)<sub>3</sub>Phen complexes:** The ternary complex of terbium(III) chloride in ethanol solution and the ligands including 1,10-phenanthroline (Phen) and SSA was synthesised according to the literature [10]. Weighed 2.73 mmol Tb<sub>2</sub>O<sub>3</sub> and 80 ml HCl (12 mol/l) in a 100 ml bottom beaker immersed in an oil bath with a magnetic stirrer, heated to 90°C to dissolve Tb<sub>2</sub>O<sub>3</sub> powder absolutely and kept the temperature to evaporate the solution to dryness, cooled to room temperature. Then the resultants were dissolved into absolute EA, finally got 0.1 mol/l TbCl<sub>3</sub> ethanol solution. Weighed 39.9 mmol SSA, 13.3 mmol Phen, 50 ml absolute EA successively in 250 ml three-neck flask immersed in a preheated oil bath (T = 80°C) with a magnetic stirrer, adjusted the pH to about 6.5 with NaOH solution (6 mol/l) after completely dissolving. At the same temperature, stirred slowly for 6 h while added 13.3 mmol TbCl<sub>3</sub> ethanol solution in dropwise, cooled to room temperature and filtrated the remains. The crude resultants were washed with EA and deionised water to remove the chloride ions, then cleaned with acetone again. Finally, the production was dried at 60°C in vacuum to constant weight.

**2.3. Preparation of thin films of PLA/Tb(SSA)<sub>3</sub>Phen composites:** Before the melt-mixing process, all materials were adequately dried in a vacuum oven at 80°C for 24 h. The mixture of PLA and Tb(SSA)<sub>3</sub>Phen with the different weight ratios was fed into the Torque Rheometer (RM-200A, Harpo Harbin Electric Technology, China), with three temperature zones of 175, 180 and 185°C, respectively, and a torque speed of 60 rpm. Then the

products were compressed into the plate of 0.5 mm thickness at 180°C by a vulcanising machine (XLB-400\*400\*2/0.25MN, Qing dao xincheng yiming Rubber Machinery Co, Ltd.) under the pressure of 5 MPa. Finally, all specimens were stored at room temperature before the analysis. The weights of each of the PLA/Tb(SSA)<sub>3</sub>Phen compositions totalled to 50.0 g. And the weight ratios of PLA to Tb(SSA)<sub>3</sub>Phen complexes were (100/0), (99/1), (97/3), (95/5) and (93/7), which were defined as PTP(100/0), PTP(99/1), PTP(97/3), PTP(95/5) and PTP(93/7), respectively.

**2.4. Characterisation:** The luminescent properties of the PLA/Tb(SSA)<sub>3</sub>Phen composite films were characterised by a fluorescence spectrophotometer (Hitachi F-7000, Hitachi High-Technologies Corp., Japan). The adopted mode was luminescence. The supplied EX slit, EM slit, PMT voltage and scan speed were set to 2.5 nm, 2.5 nm, 400 V and 1200 nm/min, respectively. All samples were tested with identical parameters and under the same conditions.

UV-vis absorption spectra of the PLA/Tb(SSA)<sub>3</sub>Phen composite films were measured with a UV-vis spectrometer (UV-5500PC, Yuanxi, China) between 150 and 800 nm.

The crystallisation behaviours of PLA/Tb(SSA)<sub>3</sub>Phen composites were investigated by a TA Instrument DSC Q200 with 3–10 mg of the samples. The measurements were carried out at a scanning rate of 10°C/min in a sealed aluminium pan under a nitrogen atmosphere with the calibration of an indium standard. At first, the samples were kept 5 min at 130°C to eliminate the thermal history and then cooled from 130 to 20°C as the first cooling run. At last the samples were again heated from 20 to 130°C for the second heating scan. Two crystallisation parameters, melt crystallisation temperature ( $T_c$ ) and onset temperature ( $T_{on}$ ) were obtained from the exothermic peak of crystallisation from the first cooling scan.  $T_{on}$  was determined by extrapolation of the exothermic peak to baseline. The half crystallisation time,  $t_{1/2}$ , was calculated by the following equation:

$$t_{1/2} = (T_{on} - T_c)/X \quad (1)$$

where  $X$  is the cooling rate (10°C/min). The crystallinity,  $\chi_c$  was calculated by the following equation:

$$\chi_c(\%) = 100 \times \Delta H_m / \Delta H_m^0 \quad (2)$$

where  $\Delta H_m^0$  is the melting enthalpy of 100% crystalline PLA (93.1 J·g<sup>-1</sup>) [11].

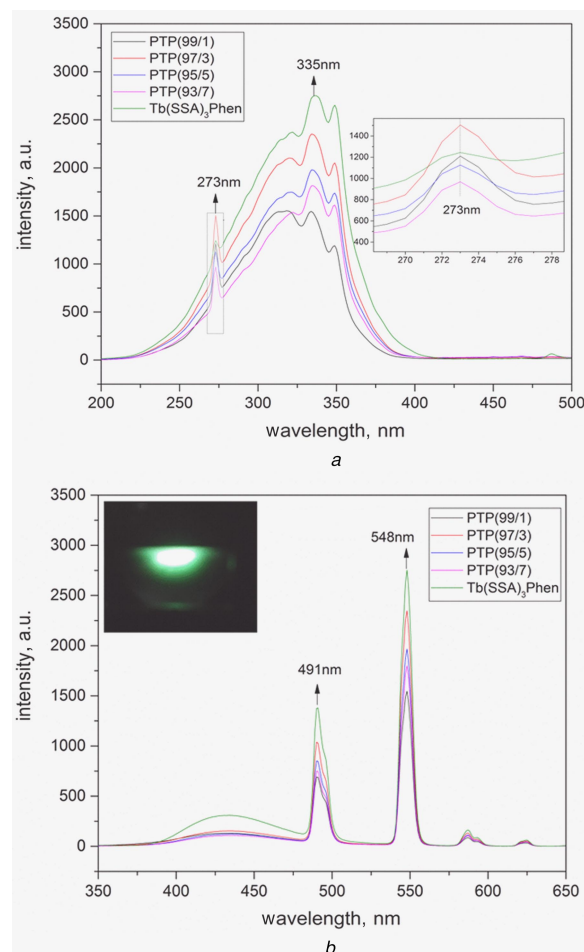
TGA of net PLA and PLA/Tb(SSA)<sub>3</sub>Phen samples was performed using a thermogravimetric analyser (Q500, TA, USA) over the temperature range 30–600°C under nitrogen atmosphere.

X-ray diffraction (XRD) patterns of PLA/Tb(SSA)<sub>3</sub>Phen samples were measured by a DX-1000 diffractometer (Dandong Fangyuan Instrument Co., Ltd, China) using a CuK $\alpha$  radiation. The voltage and current were set to 40 kV and 25 mA, respectively. Diffraction patterns were recorded for  $2\theta$  values ranging from 5 to 60° at a scanning rate of 0.06°/s.

The mechanical properties of the PLA composite films were measured using a UTM4204 universal testing machine (Sans, Shenzhen, China) with the procedures listed in the ASTM D638 standard. The specimens were prepared with dimensions of 100 × 15 × 0.1 mm<sup>3</sup>. The crosshead speed was 10 mm/min.

### 3. Results and discussion

**3.1. Photoluminescent properties:** Fig. 1*a* exhibits the excitation spectra of pure Tb(SSA)<sub>3</sub>Phen and PLA/Tb(SSA)<sub>3</sub>Phen composite films. One can see clearly that there was a broad and strong band in the wavelength region of 200–400 nm, appeared in the excitation spectrum of neat Tb(SSA)<sub>3</sub>Phen with the maxima at 335 nm. On the other hand, compared with that of Tb(SSA)<sub>3</sub>Phen, the excitation

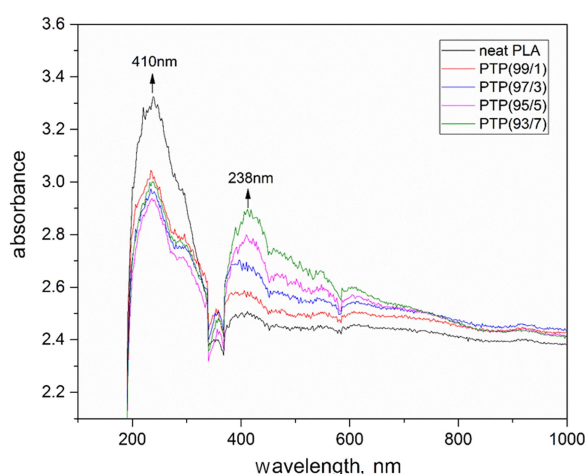


**Fig. 1** Fluorescence spectra of neat Tb(SSA)<sub>3</sub>Phen and PLA/Tb(SSA)<sub>3</sub>Phen composite films  
*a* Excitation spectra and  
*b* Emission spectra

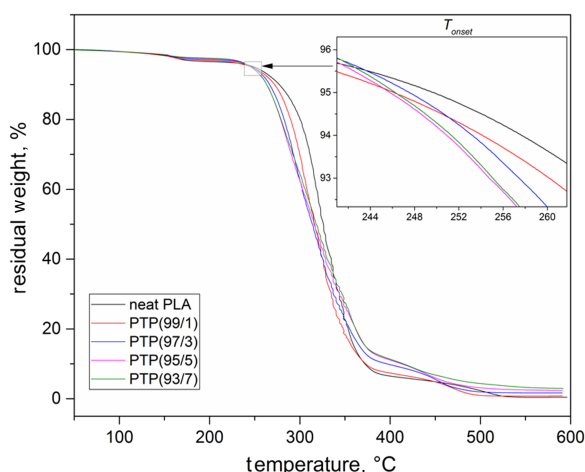
spectra of all PLA/Tb(SSA)<sub>3</sub>Phen composite samples shown the same broad bands just like Tb(SSA)<sub>3</sub>Phen, covering from 200 to 400 nm with the maxima at 335 nm. And with the increment of Tb(SSA)<sub>3</sub>Phen content, for PLA/Tb(SSA)<sub>3</sub>Phen composites the relative intensity of the maximum excitation at 335 nm increased obviously when Tb(SSA)<sub>3</sub>Phen content was increased to 3 wt%, which were weaker than that of neat Tb(SSA)<sub>3</sub>Phen. Further increased Tb(SSA)<sub>3</sub>Phen content, the counterpart of PLA/Tb(SSA)<sub>3</sub>Phen composite films just kept the slight decrease. Moreover, it was interesting that the intensity of the excitation at 273 nm became stronger than that of Tb(SSA)<sub>3</sub>Phen with the introduction of PLA. In this Letter, it implied that PLA/Tb(SSA)<sub>3</sub>Phen composites possessed luminescent properties which originated from Tb(SSA)<sub>3</sub>Phen. At the same time, the PLA matrix had a slight impact on the excitation process of the PLA/Tb(SSA)<sub>3</sub>Phen composite films. In this Letter, a plausible explanation would seem to be that the energy absorption and transfers of the Tb<sup>3+</sup> in Tb(SSA)<sub>3</sub>Phen were slightly affected by the interaction between Tb<sup>3+</sup> and the carbonyl groups of the PLA matrix.

Fig. 1*b* displays that the emission spectra of pure Tb(SSA)<sub>3</sub>Phen and PLA/Tb(SSA)<sub>3</sub>Phen composites, which was measured by the optimum excitation wavelength at 335 nm for all selective samples. It is well known that the characteristic fluorescence of Tb<sup>3+</sup> ion is light green. And the introduction of ligands such as SSA and 1,10-phenanthroline can enhance the fluorescence performance of Tb<sup>3+</sup> ion. From the emission spectra of neat Tb(SSA)<sub>3</sub>Phen, it can be found that there was a broad and intense

emission in the wavelength range from 350 to 650 nm and the maxima emission emerged at 548 nm. When  $\text{Tb}(\text{SSA})_3\text{Phen}$  was introduced into the PLA matrix, all of the PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites shown the characteristic bright green fluorescence, which belonged to  $\text{Tb}(\text{SSA})_3\text{Phen}$ . And one can see that the broader bands appeared in the range of 350–650 nm with the maxim emission at 548 nm for all PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites, just like that of pure  $\text{Tb}(\text{SSA})_3\text{Phen}$ . Additionally, the relative intensity of PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites increased monotonically with the increment of the content of  $\text{Tb}(\text{SSA})_3\text{Phen}$ , and then it gradually decreased while the  $\text{Tb}(\text{SSA})_3\text{Phen}$  content was further increased beyond 3 wt%. However, the luminescent intensities of all PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  samples were lower than that of pure  $\text{Tb}(\text{SSA})_3\text{Phen}$ . This indicates that because energy transfers of  $\text{Tb}(\text{SSA})_3\text{Phen}$  was influenced by the PLA chains, the emission



**Fig. 2** UV-vis absorption spectra of neat PLA and PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composite films



**Fig. 3** TGA thermograms of neat PLA and PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites

efficiency and the luminescent intensity of PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites can be weakened by the introduction of PLA substrate. This is in a good agreement with the results of the excitation spectra. It is noticeable that the half width of the characteristic emission peaks for all PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites was the same as that of pure  $\text{Tb}(\text{SSA})_3\text{Phen}$ , which was about 10 nm. These results demonstrated that the introduction of  $\text{Tb}(\text{SSA})_3\text{Phen}$  can endow with the photoluminescent properties for the PLA substrate.

**3.2. UV-vis analysis:** Fig. 2 shows the UV-vis absorption spectra of neat PLA and PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composite films. The broad and strong absorption band of the PLA specimen appeared in the wavelength region of 200–400 nm with the maxima at 238 nm. However, besides the absorption of the PLA substrate, the characteristic absorption of the PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites shown at the wavelength of 410 nm, which belonged to the  $\text{Tb}(\text{SSA})_3\text{Phen}$  additive. And with the increment of  $\text{Tb}(\text{SSA})_3\text{Phen}$  content its absorption intensity increased monotonously. It can also be found that the intensity of the absorption at 238 nm for the PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  films decreased markedly with the introduction of  $\text{Tb}(\text{SSA})_3\text{Phen}$ , compared with pure PLA film. This meant that the addition of  $\text{Tb}(\text{SSA})_3\text{Phen}$  would enhance the light transmittance of PLA film. Moreover, the agglomeration of  $\text{Tb}(\text{SSA})_3\text{Phen}$  as fillers was barely found, appeared as small powders in PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composite films. These results demonstrated that  $\text{Tb}(\text{SSA})_3\text{Phen}$ , which can ameliorate the PLA film transparency, are well dispersed in the PLA matrix.

**3.3. Thermal behaviours and stability:** The thermal stability of the PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites was examined by TGA in the  $\text{N}_2$  atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ . The TGA thermograms of samples are shown in Fig. 3, and the relevant data based on the TG curves are summarised in Table 1. Obviously, one can behold from the TGA thermograms that all PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composite samples exhibited the same decomposition outline as that of neat PLA. It indicated that the decomposition process of PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites was defined primarily by the PLA substrate. From Table 1, it can be found that the thermal stability of PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites was better than that of neat PLA, based on the fact that the initial decomposition temperature based on 5 wt% mass loss ( $T_{\text{onset}}$ ) of PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites were higher than the counterpart of PLA substrate. For example, pure PLA began to degrade at  $248.6^\circ\text{C}$ .  $T_{\text{onset}}$  of PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites raised up to 251.1 and  $253.1^\circ\text{C}$  with the addition of 1 and 3 wt%  $\text{Tb}(\text{SSA})_3\text{Phen}$ , respectively. When the  $\text{Tb}(\text{SSA})_3\text{Phen}$  content was beyond 5 wt%,  $T_{\text{onset}}$  of the composites almost kept the plateau. That is to say, PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites and its products can be processed and used in higher temperature before their thermal degradation. Moreover, both  $T_{50\%}$  and the residues at  $590^\circ\text{C}$  of PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites increased with the increment of  $\text{Tb}(\text{SSA})_3\text{Phen}$  content. In this Letter, it indicated that the introduction of  $\text{Tb}(\text{SSA})_3\text{Phen}$  had an evident effect on the thermal stability of the PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites.

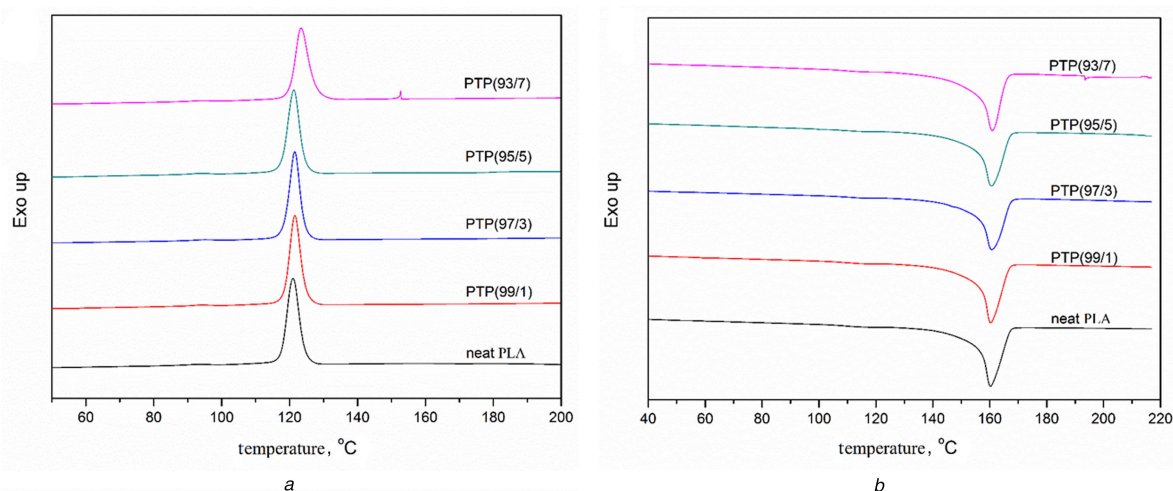
For investigating the effect of  $\text{Tb}(\text{SSA})_3\text{Phen}$  content on the crystallisation properties of PLA, the crystallisation behaviours of neat PLA and PLA/ $\text{Tb}(\text{SSA})_3\text{Phen}$  composites were examined by

**Table 1** Thermogravimetric data of neat PLA and  $\text{Tb}(\text{SSA})_3\text{Phen}/\text{PLA}$  composites in  $\text{N}_2$

Samples	Neat PLA	PTP (99/1)	PTP (97/3)	PTP (95/5)	PTP (93/7)
$T_{\text{onset}}^a, ^\circ\text{C}$	248.6	251.1	253.1	250.7	250.4
$T_{50\%}, ^\circ\text{C}$	325.9	319.1	318.6	320.9	322.4
residues at $590^\circ\text{C}$ , %	0.4	0.8	1.6	2.4	2.9

<sup>a</sup> $T_{\text{onset}}$ : the initial temperature at 5 wt% mass loss.





**Fig. 4** DSC curves of neat PLA and PLA/Tb(SSA)<sub>3</sub>Phen composites

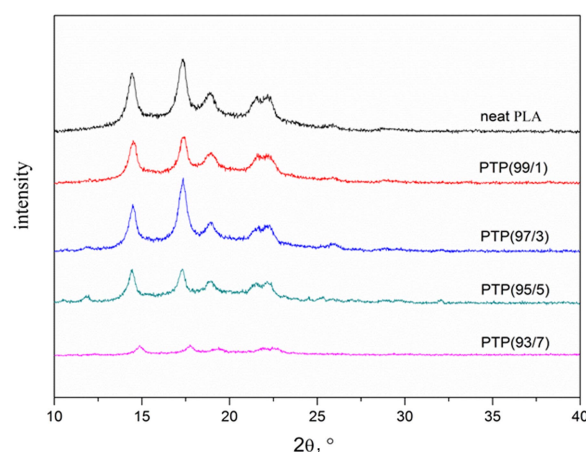
*a* Crystallisation curves at a cooling rate of 10°C/min and  
*b* Melting curves at a heating rate of 10°C/min

**Table 2** Thermal characteristics of neat PLA and PLA/Tb(SSA)<sub>3</sub>Phen composites

Samples	Cooling				Heating		
	$T_c$ , °C	$\Delta H_c$ , J/g	$T_{on}$ , °C	$t_{1/2}$ , min	$T_m$ , °C	$\Delta H_m$ , J/g	$\chi_c$ , %
Neat PLA	120.5	44.0	123.6	0.31	160.1	40.1	43.1
PTP(99/1)	121.1	43.7	123.3	0.22	160.3	38.2	41.0
PTP (97/3)	121.3	44.8	123.9	0.26	160.7	42.5	45.6
PTP (95/5)	121.9	44.3	124.9	0.30	160.6	41.4	44.5
PTP (93/7)	123.5	44.1	127.9	0.44	161.8	41.0	44.0

DSC. Fig. 4*a* presents the DSC cooling traces of the selective samples during the non-isothermal crystallisation at a cooling rate of 10°C/min. And the enthalpy data of the crystallisation exothermic peaks are listed in Table 2. One can see clearly that when Tb (SSA)<sub>3</sub>Phen was introduced into the PBS matrices, the single crystallisation peak was observed for all of the selective samples. And with the increment of Tb(SSA)<sub>3</sub>Phen content the crystallisation peak became broader than that of neat PLA. From the data of  $T_c$  (see in Table 2), we can find that when the adding content of Tb(SSA)<sub>3</sub>Phen was 1 wt%, the  $T_c$  of PLA/Tb (SSA)<sub>3</sub>Phen(99/1) sample shifted to higher temperature from 120.5 to 121.1°C, compared with that of neat PLA. And with the increase of Tb(SSA)<sub>3</sub>Phen content in PLA matrices the  $T_{cs}$  of these composites increased, the highest temperature to 123.5°C for PLA/Tb(SSA)<sub>3</sub>Phen(93/7). Therefore, this indicated that the crystalline ability of PLA/Tb(SSA)<sub>3</sub>Phen composites was influenced greatly by the Tb(SSA)<sub>3</sub>Phen content. So one can behold that the crystallisation enthalpy ( $\Delta H_c$ ) of PLA/Tb(SSA)<sub>3</sub>Phen composites increased with the increment of Tb(SSA)<sub>3</sub>Phen content. It is well known that the half time of crystallisation ( $t_{1/2}$ ) reflects the combined effect about a nucleation rate and a crystal growth rate. In Table 2, we also found that compared with that of pure PLA, the  $t_{1/2}$  of PLA/Tb(SSA)<sub>3</sub>Phen(99/1) composite decreased from 0.31 to 0.22 min with the 1 wt% addition of Tb(SSA)<sub>3</sub>Phen, which meant an increase in crystallisation rate. However, the  $t_{1/2}$  of PLA/Tb(SSA)<sub>3</sub>Phen composites increased with the increment of the Tb(SSA)<sub>3</sub>Phen content when beyond 3 wt%, shown a confinement effect during the crystallisation process. In this work, it could be said that the nucleation effect of composites depends on the concentration of Tb(SSA)<sub>3</sub>Phen complex and a proper amount of Tb(SSA)<sub>3</sub>Phen would accelerate the crystallisation of PLA.

To further analyse, the thermal behaviour of the selective samples, the samples were heated again at a heating rate of 10°C/min after non-isothermally crystallisation at the cooling rate of 10°C/min. The DSC heating curves of pure PLA and PLA/Tb (SSA)<sub>3</sub>Phen composites are shown in Fig. 4*b*, and the data of the melting temperature ( $T_m$ ) and the melting enthalpy ( $\Delta H_m$ ) are summarised in Table 2. Similarly, the  $T_{ms}$  and the  $\Delta H_{ms}$  of the composites increased with the increase of Tb(SSA)<sub>3</sub>Phen content, which was in good agreement with the non-isothermal crystallisation behaviour of the samples. In this Letter, it could be explained that during the crystallisation process of the PLA matrix, the Tb



**Fig. 5** XRD patterns of neat PLA and PLA/Tb(SSA)<sub>3</sub>Phen composite

**Table 3** Degree of crystallinity of PLA and PLA/Tb(SSA)<sub>3</sub>Phen composites

	PLA	PTP (99/1)	PTP (97/3)	PTP (95/5)	PTP (93/7)
degree of crystallinity, %	27.6	24.7	33.8	23.1	18.3

**Table 4** Mechanical properties of PLA/Tb(SSA)<sub>3</sub>Phen composite films

Samples	Tensile strength, MPa	Young's modulus, MPa	Elongation at break, %
neat PLA	19.3 ± 0.13	780.8 ± 1.2	34.9 ± 15.4
PTP(99/1)	19.4 ± 0.12	854.0 ± 1.4	13.4 ± 15.3
PTP (97/3)	19.6 ± 0.13	1020.8 ± 1.3	10.1 ± 13.2
PTP (95/5)	19.0 ± 0.15	990.7 ± 0.9	8.1 ± 16.9
PTP (93/7)	18.2 ± 0.10	882.0 ± 0.8	8.0 ± 10.1

(SSA)<sub>3</sub>Phen complex acts as the nucleating agent, which can improve the crystallisation behaviours of PLA. So the degree of crystallinity ( $\chi_c$ ) of PLA/Tb(SSA)<sub>3</sub>Phen composites increased with an increase of the Tb(SSA)<sub>3</sub>Phen content.

**3.4. XRD analysis:** Fig. 5 exhibits the XRD patterns of pure PLA and PLA/Tb(SSA)<sub>3</sub>Phen samples and the degree of crystallinity calculated based on XRD data are listed in Table 3. All samples were stored at 40°C in a vacuum oven for 48 h before testing. PLA had narrow and sharp peaks at  $2\theta = 14^\circ$ ,  $16^\circ$ ,  $19^\circ$  and  $22^\circ$ , respectively. It clearly shows that there were no obvious differences at the diffractograms of neat PLA and PLA/Tb(SSA)<sub>3</sub>Phen samples. However, the peak intensity of PLA/Tb(SSA)<sub>3</sub>Phen composites increased with the increment of the Tb(SSA)<sub>3</sub>Phen content in the range from 1 to 3 wt%. When it was beyond 3 wt%, the intensity of the composites decreased gradually. It indicated that the presence of Tb(SSA)<sub>3</sub>Phen had a distinct effect on the degree of crystallinity of the samples. For example, 1 wt% of Tb(SSA)<sub>3</sub>Phen decreased the degree of crystallinity of PTP(99/1) by 2.9% from 27.6% of pure PLA to 24.7%. However, when the adding content of Tb(SSA)<sub>3</sub>Phen was 3 wt%, the degree of crystallinity for the PTP(97/3) sample increased by 6.2% in contrast with that of pure PLA. And while it was beyond 3 wt%, the degree of crystallinity for the selective samples decreased gradually. It is in a good agreement with DSC results above.

**3.5. Mechanical properties:** To assess the effect of Tb(SSA)<sub>3</sub>Phen on the mechanical properties of the PLA matrix, the tensile test of the composite films were investigated. The values for tensile strength, Young's modulus and elongation at break of the PLA/Tb(SSA)<sub>3</sub>Phen composite films are summarised in Table 4. From the data, we found that the tensile strength and Young's modulus almost progressively increased with the increment of Tb(SSA)<sub>3</sub>Phen content in the earlier stage from 1 to 3 wt%. It indicated that there is a good interfacial adhesion between the PLA matrix and Tb(SSA)<sub>3</sub>Phen. As we know, the similar increase in the mechanical properties has been observed in other nanocomposites such as PLA/clay, PLA/silica, and PLA/MWCNT. Therefore, the amount of Tb(SSA)<sub>3</sub>Phen had a direct influence on the mechanical properties of the PLA matrix. When it was beyond 3 wt%, the values of tensile strength and Young's modulus reduced gradually. At the same time, the value of elongation at break decreased obviously when Tb(SSA)<sub>3</sub>Phen content was increased to 3 wt%. Further increased Tb(SSA)<sub>3</sub>Phen content, the values of elongation at the break just kept the slight decrease. This indicated that the excessive amount of Tb(SSA)<sub>3</sub>Phen was not beneficial for improving the mechanical

properties of the PLA. In this Letter, it can be explained that the excessive amount of Tb(SSA)<sub>3</sub>Phen additive could become close enough together to agglomerate into larger particles.

**4. Conclusion:** Tb(SSA)<sub>3</sub>Phen was synthesised based on terbium (III) (Tb<sup>3+</sup>) ion and the ligands including Phen and SSA. And PLA composite films containing Tb(SSA)<sub>3</sub>Phen were prepared by the melt-mixing process. The luminescent and optical properties of PLA/Tb(SSA)<sub>3</sub>Phen composite films were investigated by fluorescence spectrophotometry and UV-vis spectrometer. The introduction of Tb(SSA)<sub>3</sub>Phen can not only endow with the photoluminescent properties for the PLA substrate but ameliorate the PLA film transparency which well dispersed in the PLA matrix. Effect of addition of Tb(SSA)<sub>3</sub>Phen on thermal behaviours, crystal structure and mechanical properties of PLA was investigated by TGA, DSC, XRD and universal testing machine. The addition of Tb(SSA)<sub>3</sub>Phen influenced the thermal behaviours of PLA.  $T_{onset}$  of PLA composites was improved by introducing a Tb(SSA)<sub>3</sub>Phen complex. And the degree of crystallinity and the crystallisation rate of PLA composites increased with an increase in a certain range of Tb(SSA)<sub>3</sub>Phen content. From XRD data analysis, though the adjunction of Tb(SSA)<sub>3</sub>Phen in composites had no significant effect on the crystalline parameters of the PLA matrix, the presence of Tb(SSA)<sub>3</sub>Phen influenced on the degree of crystallinity of the PLA composites. The tensile strength of the PLA composite films was enhanced by the addition of Tb(SSA)<sub>3</sub>Phen, i.e. 1 and 3 wt%.

**5. Acknowledgments:** This work was financially supported by (1) the Science and Technology Project Affiliated to Chongqing Municipal Education Department (grant no. KJ1601121); (2) the Natural Science Foundation of Yongchuan District Science and Technology Commission, Chongqing, China (grant no. 2016nc1001, Ycstc); and (3) the Student's Platform for Innovation and Entrepreneurship Training Program of Chongqing Municipal Education Department (grant no. 201610642278).

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