Fluorescence Properties of Bio-based PA/Eu (TTA)₃phen Fibers

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Abstract. Bio-based polyamides and europium complex Eu(TTA)₃Phen were mixed and the PA/Eu(TTA)₃phen composite fibers were prepared by melt spinning method. XRD and DSC curves indicated that a coordination bond was formed between PA and Eu(TTA)₃Phen complex. The results of fluorescence spectra showed that the composite fibers displayed intense characteristic fluorescence emission in the red region of the spectrum of Eu³⁺ ion at room temperature, and the energy transfer between rare earth complexes and the matrix was good. With the increasing of rare earth complex added into the PA matrix, the fluorescence intensity increased accordingly, when the content was up to 12wt%, the ‘concentration quenching’ emerged.

1. Introduction

Polyamide is the earliest synthetic fiber developed and industrialized in the world. Many excellent properties of polyamide determine its wide application[1-2], especially in apparel and apparel products. Therefore, the development of high-value-added products and new manufacturing processes that give full play to the specialty of polyamide are ongoing. In the research of functional polyamide, because the use of rare earth organic ligand composite materials is a hot spot in material science and has a very broad prospect, it is a new subject to prepare fluorescent materials of polyamide matrix by compounding rare earth organic complexes into polyamide matrix, which is rarely reported in the literature.

The polyamide matrix used in this project is a new type of bio-based polyamide[3]. Under the current requirements of energy and environment, the development and production of bio-based macromolecule materials conforms to the concept of sustainable development and circular economy. The research on bio-based polyamide fibers is of great significance to the development of textile industry.

Rare earth complex was added into the self-made bio-based polyamide matrix, and the rare earth/polyamide fibers were prepared by melt-spinning. Luminescence characteristics of the rare earth/polyamide fibers were discussed in detail, which provided a reference for the development of rare earth/new bio-based polyamide functional materials.

2. Experimental

2.1 Materials

Eu₂O₃ powder with 99.99% purity was bought from Beiyanxincai Company. Polyamide was synthesized by melt-condensing IA, SA, BD, and DD at the mol ratio of 1:1:1:1[3]. The average molecular weight of PA is 78000, and the polydispersity coefficient is 1.80. Other reagents used in this paper were commercially available analytical grade.
2.2 Preparation of PA/Eu (TTA)₃phen fibers
Eu₂O₃ was dissolved in concentrated hydrochloric acid and purified to form EuCl₃ crystal. EuCl₃ was then mixed with alpha-methylthiophene trifluoroacetone (TTA) and 1,10-phenanthroline (Phen) in a molar ratio of 5:3:1 to obtain Eu (TTA)₃Phen. Composite fibers were obtained by melt spinning of Eu (TTA)₃Phen and bio-based polyamide.

2.3 Characterization
The X-ray diffraction analysis was performed by the Rigaku D/Max-IIIC diffractometer of Nippon Science and Electricity Company, the radiation source of Cu/K alpha radiation, the working voltage of 20KV, the current of 200mA, are used for continuous scanning. The scanning range is 5-50 degrees and the scanning rate is 5°/min.

The DSC thermogram was recorded using a STARe system DSC1 Instruments (Mettler-Toledo, Switzerland) at a heating rate of 10 °C/min. The N₂ flow rate was 150 mL/min.

The 612 nm excited state fluorescence lifetime was measured using a Nd3T:YAG (yttrium aluminum garnet) pulsed laser excitation 346 nm steady state and lifetime fluorometer (FL3-2-IHR221-NIR-TCSPC, Horiba Jobin Yvon Inc).

The fluorescent spectra of the fibers were recorded by a Hitachi F-4500 Fluorescent spectrometer with excitation. The width of the emission slit was 2.5nm. The scanning voltage is 400V and the scanning speed is 1200nm/min.

3. Results and discussion

3.1 Thermal and Crystalline Properties

![Figure 1](image_url)

Figure 1. Figure with short caption (caption centred).

| Eu(TTA)₃Phen content(%) | Crystallinity (%) |
|-------------------------|-------------------|
| 0                       | 65                |
Figure 1 gives XRD spectra of pure PA and composite fibers, and detailed data on crystallinity are shown in Table 1. Diffraction peaks of the Eu(TTA)$_3$Phen complex are obvious with characteristic crystal diffraction of 2θ=31° and 45°, indicating the crystal of Eu(TTA)$_3$Phen complex have formed.

With the increasing content of the complex added to the PA matrix, the crystal form transformed gradually from γ-crystalline phase with single diffraction peak at 2θ=21° to α-crystalline phase with double diffraction peaks at 2θ=20° and 23°, which may be due to the good dispersibility of Eu(TTA)$_3$Phen complexes, while the crystallinity of fibers decreased from 65% to 44% (as shown in Table 1), which indicated that the added complex hindered the behavior of crystallization within PA resulting from the strong interaction between the complexes and the macromolecular chains of PA[4]. The results back up the fact that complex clusters have been generated inside the matrix, undermining chain structure regularity, thus the crystallinity of composites declined accordingly. As the complex doping content comes to 12%, PA composite materials virtually turn into amorphous structure.

In addition, as shown in the spectrum, when the mass ratio of Eu(TTA)$_3$Phen reaches no less than 5%, the characteristic crystal diffraction of Eu(TTA)$_3$Phen (2θ=31°) can be obviously observed.

The introduction of Eu(TTA)$_3$Phen could affect not only the crystallization behavior but also the thermal behavior of the PA composite fibers. Figure 2 shows the glass transition process of PA melt-spun fibers using differential scanning calorimetry (DSC) measurements. With the increase of Eu(TTA)$_3$Phen complexes content, the glass transition temperature (Tg) of PA showed a remarkable increase. The Tg of PA composites increased from 44.1°C to 51.9°C progressively when Eu(TTA)$_3$Phen content increased from 1wt% to 12wt%, owing to the coordination of the carbonyl groups of PA and Eu(TTA)$_3$Phen complexes. Meanwhile, the coordination restricted the movement of PA chain segments.

3.2 luminescent properties
Figure 3. DSC spectra of pure PA and fibers.

Luminescent properties of the PA/Eu(TTA)_3phen melt-spun fibers were investigated, and the results are shown in Figure 3. The wide range of features observed at lower wavelengths represent the effective antenna effect between ligands and Eu³⁺ ions. In the pure Eu(TTA)_3Phen complex, a broad excitation band from 240 to 460 nm appears, which is related to the π-π* electron transition of the ligands[5]. The splitting of the excitation band into two components can be observed in the composites, which indicates that the position symmetry of Eu³⁺ ions in the composite fibers decreases due to the influence of the macromolecular chains of PA. The wide excitation band centered at 340 nm is attributed to charge transfer of PA-Eu[6]. The broad excitation bands centered at 340 nm are ascribed to PA-Eu charge transfer. These peaks become much raised in the spectrum of the composite fibers, which suggests numerous PA-Eu bonding were formed which indicated that the matrix PA promotes the excitation process for the composite materials. The result is consistent with the above-mentioned findings. In addition, the excitation of 7F0-5D2 and 7F1-5D1 disappeared, indicating that the f-f inner shell transition of fibers replaced the non-radiative relaxation from high excitation state to 5D0 by non-radiative energy transfer from higher excitation state to organic matter or horizontal quenching of some unrecognized defects.

All emission spectra are similar and have the same spectral characteristics. They consist of several bands associated with the excitation of the Eu³⁺ ion 5D0 excitation level. They are mainly controlled by a sharp red band emission at ~610 nm, which is a typical Eu³⁺ emission due to the 5D0→7F2 transition. In addition, weak emission bands of 587 and 595 nm are also shown in the emission spectrum, which are 5D0→7F0 and 5D0→7F1 transitions, respectively. The results show that the ligand or coordination group has a good sensitization effect on Eu³⁺ ions, and shows high intensity, narrow half-width and monochromatic light photoluminescence. There was no fluorescence emission by substrate, which appeared around 400 nm in the pure PA according to Figure 7(B). Apparently there should be existing competition for light absorption between Eu(TTA)_3Phen and substrate.

The intensity ratio between 5D0 → 7F2 to 5D0 → 7F1 (I02/I01) is usually used to measure the asymmetry of Eu³⁺ ions. The content of Eu(TTA)_3Phen was calculated to be 1, 5, 8, and 12 wt %, and the proportions were 9.00, 9.99, 10.01 and 10.51, respectively. The results show that the local environment around Eu³⁺ ions is more disordered, and the addition of more complexes in PA matrix leads to the polarization of Eu³⁺ ions, which further leads to a higher probability of electron dipole transition, accounting for the increasing in luminescent intensity of the 613 nm peak.

3.3 Luminescence Decay Times (τ)
Figure 4. The decay curves of the complex and fibers.

Table 2. The luminescence lifetimes of Eu(TTA)$_3$Phen and fibers.

| Sample | Eu(TTA)$_3$Phen | fibers with different Eu(TTA)$_3$Phen weight contents |
|--------|-----------------|------------------------------------------------------|
|        |                 | 1% | 5% | 8% | 10% | 12% |
| luminescence lifetimes /μs | 771 | 678 | 880 | 1050 | 1063 | 884 |

The luminescence decays for both PA/ Eu(TTA)$_3$Phen fibers and Eu(TTA)$_3$Phen can be fit by single exponentials as \( I = I_0 \exp\left(-t/\tau\right) \), where \( \tau \) is the 1/e lifetime of Eu$^{3+}$ ions, which indicates that all of the Eu$^{3+}$ ions have similar environment within the composite fibers, from which the luminescence lifetimes were calculated and listed in Table 2.

It can be seen from the Table 2, the exponential lifetimes obtained for the 5D0 states was 771μs in the pure complex, and 678μs, 880μs, 1050μs, 1063μs, 884μs corresponding to PA/Eu(TTA)$_3$Phen composite fibers with various mass concentrations (1%, 5%, 8%, 10%, 12%) of complex. Generally, the fluorescence lifetime of the 5D0 state in the fibers increased compared with that in the pure Eu(TTA)$_3$Phen complex, which indicated that PA polyamide is an excellent host to these complexes. Fluorescence spectra of pure complexes and the fibers indicated changes in the environment surrounding the chelated Eu$^{3+}$ ions. In the case of a pure complex, the chelating Eu$^{3+}$ ionic environment was homogeneous and the ligand was limited to the fine-grained framework of the complex.

However, in the case of composite materials, the composite molecules were dispersed in the PA matrix. The release of the Eu(TTA)$_3$Phen complex is based on efficient energy transfer from adsorption of organic ligands to chelation of Eu$^{3+}$ ions. On the other hand, in the excited state, the vibration of the ligand and the lattice causes non-radiative transitions of certain energies, thereby reducing the fluorescence lifetime. The relatively rigid structure of the PA matrix limits the above vibrations,
reducing non-radiative transitions, thereby increasing the lifetime of the composite in the PA matrix[7]. When the content was up to 12w%, the ‘concentration quenching’ emerged. With the more Eu(TTA)3Phen complex added to the matrix, the nonradiative transition rate from 5D0 to 7FJ increase because of the emerging of fluorescence quenching, which may lead to a shorter fluorescence lifetime.

4. Conclusion
In this work, PA/Eu(TTA)3Phen fibers were prepared by melt-spinning. In the composite materials, a large number of coordination bonds PA-Eu are formed between the carbonyl groups of PA and EU(TTA)3, which contributes the good luminescent properties of composite fibers. The fluorescent intensity increased with increasing Eu(TTA)3Phen complex concentration and saturated at 12wt%. In the meantime, the luminescence lifetime was extended accordingly, which indicated that the energy transfer between rare earth complexes and the matrix was good.

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