Structure and Properties of Melt-spun Bio-based Polyamide/Eu(TTA)$_3$Phen Composite fibers

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Abstract. In this paper, the bio-based polyamide (PA) was melt polymerized from four bio-based monomers. Composites of the bio-based PA and europium complex Eu(TTA)$_3$Phen were prepared through solution mixing using N, N-Dimethylformamide (DMF) and formic acid as the mixed solvent, and then composite fibers were obtained by melt spinning method. The structure and properties of the melt-spun composite fibers were characterized by FTIR and SEM. The results indicated that the Eu(TTA)$_3$Phen complex, with the average diameter below 300 nm, was homogeneously dispersed in the PA matrix. FTIR spectra indicated that the coordination bond between carbonyl of BDIS and Eu(TTA)$_3$Phen complex formed, which was also confirmed by the mechanical properties. The initial modulus and breaking strength of these fibers can arrived at 2.5GPa and 0.3GPa, respectively.

1. Introduction
During the past decades, much attention was paid on the trivalent rare earth ions due to their unique emission properties from the intra-4f transitions, which are shielded by outer 5s5p orbital [1]. The incorporation of rare earth organic complexes into polymer matrixes can combine the characteristics of both the complexes and polymers, can display high lighting properties, good processing abilities, chemical stabilities, and good mechanical strengths, making them applicable in the areas of optical, electrical, magnetic materials [2, 3]. To date, the potential applications of the polymer-capped rare earth complexes in display, probes, and laser materials have been conducting extensive research [4-6].

Polymer-capped rare earth complexes can be prepared by physical blending and chemical incorporation. Physical blending can be easily achieved through melt blending, mechanical blending, or solution mixing, which is simple and convenient. With the increasing content of complexes added into the polymer matrixes, it becomes more difficult to prepare a uniformly distributed polymer-capped rare earth complexes because of the intermolecular aggregation of complexes and the poor solubility of rare earth complexes in the polymer matrices [7, 8].

In this paper, we used N, N-Dimethylformamide (DMF) and formic acid as the mixed solvent during the preparation of the composites to ameliorate this situation. Furthermore, homogeneous mixing of the complexes in the bio-based PA matrix could be achieved by virtue of the large solubility of the Eu(TTA)$_3$Phen into DMF. The aim of this study was to search a simple and feasible method for increasing the concentration of rare earth complexes into the bio-based PA, and at the same time, to improve the mechanical properties of materials.
2. Experimental

2.1. Materials
All the materials used in this paper are listed in Table 1.

| samper             | purity   | provider                        |
|--------------------|----------|---------------------------------|
| Eu₂O₃ powder       | 99.99%   | Haimen Material Technology Co., Ltd |
| Itaconic acid (IA) | 98%      | Alfa-Aesa                       |
| Sebacic acid (SA)  | 98%      | Alfa-Aesa                       |
| 1,4-diaminobutane (BD) | 98%   | Alfa-Aesa                       |
| 1,10-diaminodecane (DD) | 98%   | TCI-EP (Tokyo)                  |
| others             | AR       | Commercial available            |

Four monomers (IA, SA, BD, and DD) are melt polymerized to produce the bio-based PA. In the polymerization, mol ratios of four monomers are same. Here the bio-base PA has $M_n$ of 70000, and a polydispersity index of 1.80.

2.2. Preparation of Europium Complex, Eu(TTA)₃Phen
Eu₂O₃ (0.0125mol) was dissolved in HCl followed by successively evaporating the excessive acid, and then dissolved in the ethanol, and moved to a 250 ml sidearm flask. 2-Thenoyltrifluoroacetone (0.075mol) and 1,10-phenanthrolinec (0.025mol) ethanol solution were dripped to the flask, respectively. The mixture was under a continue stirring at 60 °C with a time of 5h. Then the solutions were cooled at a room temperature, and its pH value was adjusted to 6~7 by ammonia. The system was allowed to stand overnight. After the filtering and washing with ethanol, the precipitate was obtained and dried standby. Its chemical formula as Eu(TTA)₃phen was proved by the elementary analysis.

2.3. Melt-spinning of PA/Eu(TTA)₃phen fiber
The composite with 1wt% Eu(TTA)₃Phen content in bio-based PA was prepared as follows. First, 20g of the bio-based PA was dissolved into 20ml formic acid and 0.202g Eu(TTA)₃Phen was dissolved into 30mL DMF, after completely dissolving, mixed the two solutions together, stirred for 6h under 60 °C, and then evaporated to dryness. In this paper, the weight content of Eu(TTA)₃Phen in the composite is variable, 5 %, 8 %, and 12 %, respectively. Then the fibers were prepared by the melt-spinning method. Those fibers were stretched to a optimum ratios at 130°C, and heat-set at 140°C.

2.4. Characterization
For all sample, Fourier Transform Infrared spectra in the range of 2000-500 cm⁻¹ was completed on a NEXUS FT-IR spectrophotometer. Scanning electron micrographs (Cambridge S-250-III) was used to character the dispersion of rare earth in the PA matrix. The mechanical properties of PA/Eu(TTA)₃phen fibers were achieved by Instron 5969 according the ASTM standard.

3. Results and discussion

3.1. Morphology of the composite fibers
SEM images in Fig. 1 show the morphology of cross-section of composite fibers with various mass ratios 1%, 5%, 8% and 12% of Eu(TTA)₃Phen. It can be observed that the Eu(TTA)₃Phen complex particles were well dispersed in the polymeric matrix with dimension about 100-300 nm, which was smaller than their original sizes. one possible reason for this obvious decrease in size of
Eu(TTA)$_3$Phen particles is that due to the complexation effect between Eu(TTA)$_3$Phen complex particles and PA matrix, moreover, the mechanical agitation and shearing effects during the processes of melt spinning improved the disperse state of Eu(TTA)$_3$Phen in PA.

Figure 1. SEM photos of the PA composite fibers containing different contents of Eu(TTA)$_3$phen complex (a)1wt%, (b)5wt%, (c)8wt%, (d)12wt%, and (e) Eu(TTA)$_3$phen complex.

3.2. Interaction between RE and PA
The IR spectra (1000–2000 cm$^{-1}$) of the bio-based PA/Eu(TTA)$_3$phen composites and pure bio-based PA are shown in Fig.2. In the spectrum of pure PA, the band at 1635 cm$^{-1}$ (Amide I, C=O stretch) and 1542 cm$^{-1}$ (Amide II, C-N stretch + CO–N–H bend) are assigned to the characteristic vibrational modes of PA. The characteristic peaks of composite fiber shift to higher wavenumber, which may be caused by the coordination bond formed between the carbonyl of the PA and Eu$^{3+}$ ions. These indicate that PA, acting as a lewis base, its carbonyl oxygen atoms and the nitrogen atoms of the amide bond in the polymer chain tend to share a free-electron pair with the f electron orbits available from Eu$^{3+}$ ions and form coordination bond.
Figure 2. FTIR spectra of pure PA and PA/Eu(TTA)$_3$phen composite fibers.

3.3. Mechanical properties

Figure 3. Stress-strain curves of PA and the composite fibers with various contents of Eu(TTA)$_3$Phen.

Fig.3 shows the typical stress-strain curves of PA and the composite fibers doped with different contents of Eu(TTA)$_3$phen complex. Inset shows the enlarged initial portion of all these curves. Detailed mechanical property results of PA with different weight ratios of Eu(TTA)$_3$Phen are listed in table 3. From the shape of these curves and the specific data we can deduce that the materials exhibit a trend of being much more unyielding and stronger progressive, and transform from ductile fracture to brittle rupture (when weight ratio of Eu(TTA)$_3$Phen comes to 12%). Meanwhile, as is shown in table 3, the initial modulus of composite fibers increases from low Eu(TTA)$_3$Phen complex content, and reached a maximum. Similar trend is found in the change of breaking strength values. When Eu(TTA)$_3$Phen complex content reaches 8 wt%, the maximum modulus and breaking strength of the composite fibers were 2504.0 and 305.8MPa, respectively.

There are plenty of explanations for the reinforcement mechanism. According to the above characterizations, the reasons may be listed as follows: firstly, good compatibility between PA and Eu(TTA)$_3$Phen leads to the nice dispersion of the dopant in the matrix, in addition, within the interpenetrating polymeric network structure of the composite fibers, the coordination bond can transfer and distribute the applied stress of molecular chains. However, when the Eu(TTA)$_3$Phen
content comes to 12%, much aggregations of the complex result in stress concentration of composite fibers, the mechanical properties deteriorated accordingly.

4. Conclusions
In this work, the bio-based PA/Eu(TTA)$_3$Phen fibers were successfully obtained through melt-spinning. Within the composite materials, a considerable amount of the coordinate bond PA-Eu$^{3+}$ between carbonyl of PA and Eu(TTA)$_3$Phen complex was formed, the rest of complexes dispersed in the matrix with a dimension smaller than 300 nm. The maximum initial modulus and breaking strength of composite fibers obtained were 2504.0 and 305.8MPa, respectively, when Eu(TTA)$_3$Phen content was 8 wt%, which improved significantly compared with pure PA.

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