Influence of triarylsulfonium hexafluoroantimonate on spectral characteristics of luminous polypropylene/ $SrAl_2O_4$: Eu^{2+}, Dy^{3+} fiber

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A luminous polypropylene/$SrAl_2O_4$: Eu^{2+}, Dy^{3+} fiber was prepared by the way of melt-spinning method which uses triarylsulfonium hexafluoroantimonate (TSHF), organic silicon-modified luminescent materials and polypropylene substrate to produce a new luminous material with blue-light emission in the darkness. The effect of TSHF on emission luminescence properties was studied by analyzing the afterglow brightness, emission spectral and colorimetric characteristics. The results indicate that the spectral characteristics of the fiber were mainly determined by the energy transfer from TSHF to $SrAl_2O_4$: Eu^{2+}, Dy^{3+} powder. When the doping amount of TSHF reached 0.5 wt%, the emission wavelength of the fiber began to shift toward the blue region.

(Received April 22, 2019; accepted April 9, 2020)

Keywords: Triarylsulfonium hexafluoroantimonate, $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphor, Luminous polypropylene fiber, Spectral

1. Introduction

In recent years, luminous fibers have attracted considerable interest owing to their desirable afterglow performance. Luminescent materials such as $SrAl_2O_4$:Eu^{2+}, Dy^{3+} have been used in melt-spinning processes to fabricate synthetic fibers with excellent luminescent properties, while other spinning methods are rarely used in the fabrication processes [1-5]. Due to the required micron-level particle size of the material and the very low brightness of the micron-sized luminous powder, other spinning methods such as bubble-electrospinning cannot meet the specifications of application.

Owing to the advantages of superior afterglow properties, UV radiation resistance and chemical stability, the $SrAl_2O_4$:Eu^{2+}, Dy^{3+} luminous fibers have been studied extensively. The emission spectrum of the luminous fibers is distributed in the yellow-green region with an emission peak at 510-530 nm, and the emission colors in this region are monotonous and lacks red light and blue light. The blue-light luminous fibers are usually prepared by directly by using materials with long blue afterglow or by addition of blue pigments. However, the luminescent performance of the blue-light emitting materials supplemented with blue pigments is poor, limiting their application in the real production [6]. In addition, the lattice structure of blue-light emitting materials (mainly $CaAl_2O_4$ and $BaAl_2O_4$) and the energy level transitions of rare earth ions lead to poor luminescent properties, which results in undesirable outcomes in various fields of applications. The above drawbacks represent the bottleneck for the research and the development of blue-light luminous fibers.

Triarylsulfonium hexafluoroantimonate (TSHF) is an aromatic organic luminescent compound. It absorbs visible and ultraviolet light and emits light at a specific wavelength. TSHF is extremely important for the regulation of luminescent color, and possesses broad absorption spectrum, superior fluorescence quantum yield and relatively stable light-emitting properties [7]. At present, the research and development of TSHF is mainly limited to the fabrication of light curing adhesives [8], UV curable coatings [9,10], photocurable inks [11] and photocurable electronic packaging materials [12,13]. Meanwhile, few studies have explored the interactions between TSHF and the rare earth luminescent materials [14]. In this work, the organic luminescent compound TSHF was incorporated into the rare earth aluminate luminescent fiber. The organic luminescent compound TSHF not only plays the role of adjusting the color of the strontium aluminate luminous fibers, but also increases the light conversion efficiency of the fiber luminescent center. Therefore, the results of this study provide theoretical and practical basis for the application of rare earth luminescent materials and strontium aluminate-based luminous fibers. Meanwhile, the findings show an important scientific significance and draw an attractive prospect of commercial applications.

In this study, the influence of TSHF on spectral characteristics was investigated to deep improve the understanding of energy transfer mechanism in luminous polypropylene fibers containing TSHF. The results obtained in this work establish the theoretical and technical foundation for the development of luminous fibers.

2. Experimental

2.1. Sample preparation

The fibers were prepared using KH550 modified $SrAl_2O_4:Eu^{2+}$, Dy^{3+} powder, TSHF and polypropylene (PP) chips. The $SrAl_2O_4:Eu^{2+}$, Dy^{3+} powder was produced by microwave calcination using $SrCO_3$, Al_2O_3, Eu_2O_3, Dy_2O_3 and H_3BO_3 as raw materials. The raw materials were ground together in a ball mill to give a homogeneous mixture, the resulting powder was annealed at 1400 ℃ for 4 h in a carbon reducing atmosphere, and finally the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} power was synthesized. The detailed manufacturing procedure of the powder is described in Table 1.

The surface of the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} powder was characterized by facile adsorbance of a water film layer, which affected the luminescent properties. A silane coupling agent (KH550) was used to react with the hydrophilic hydroxy groups to form SiO-M covalent bonds. At the same time, the silanol groups of the silane were associated with each other to form a network-like film, which could cover the surface of the luminous particles. Therefore, the chemical modification of luminescent powders can prevent their hydrolysis. The phosphors were treated with an appropriate amount of KH550 silane coupling agent, stirred, washed 3 times with absolute ethanol, and finally dried to obtain the KH550 modified phosphors. Subsequently, the PP chips were dried and then mixed with an appropriate amount of KH550 modified phosphors. Next, TSHF and spinning auxiliaries were put in a high-speed mixer with the spinning temperature set at 220-250℃ and the draw ratio set at 2.9. Finally, the mixtures were melted and spun to obtain the fibers. The key manufacturing information is given in Table 2.

Table 1. Manufacturing method of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} powder

Raw material	Molar ratio	Microwave temperature/(℃)	Microwave power/(w)	Microwave time/(h)	Cooling mode
$SrCO_3$ Al_2O_3 Eu_2O_3 Dy_2O_3 H_3BO_3	Sr：Al：Eu：Dy =1：2：0.025:0.025，The addition of H_3BO_3 is 5% of the total volume of the mixture (molar ratio)	1400℃	900W	2h	Natural cooling

Table 2. Manufacturing method of luminous fibers by doping with triaryl sulfonium hexafluoroantimonate (TSHF)

Sample	The mass ratio of raw material formula		
	PP	The Modified $SrAl_2O_4:Eu^{2+}$, Dy^{3+}	TSHF
1#	95%	5%	0%
2#	94.7%	5%	0.3%
3#	94.6%	5%	0.4%
4#	94.5%	5%	0.5%
5#	94.4%	5%	0.6%
6#	94.3%	5%	0.7%
7#	100%	0%	0%

2.2. Measuring methods

The micromorphology and composition were studied using a scanning electron microscope (SEM) (Quanta 200). The afterglow decay properties were analyzed by the PR-305 Long-ray Fluorescence Tester. The excitation and emission spectra were recorded using a fluorescence spectrophotometer (Hitachi 650-60, Japan). Chromaticity diagrams were recorded by the PR-650 SpectraScan Colorimeter.

3. Results and discussions

3.1. Surface morphology

The micrographs of the phosphor and luminous fibers are presented in Fig. 1 (a1)-(c2). As shown in Fig.1 (a1), the particle size of the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} powder was mainly between 1-8 μm, and the powder exhibited irregular polygonal shapes with more pronounced agglomeration phenomenon in comparison with that in Fig.1 (a2). Nevertheless, as illustrated in Fig. 1 (a2), the surface of particle was significantly improved modified by KH550 and became rounded to a certain extent. Moreover, the KH550 contains two different reactive groups (amino and oxy), which are used to couple organic and inorganic fillers and improve the wettability and dispersibility of the filler in the polymer.

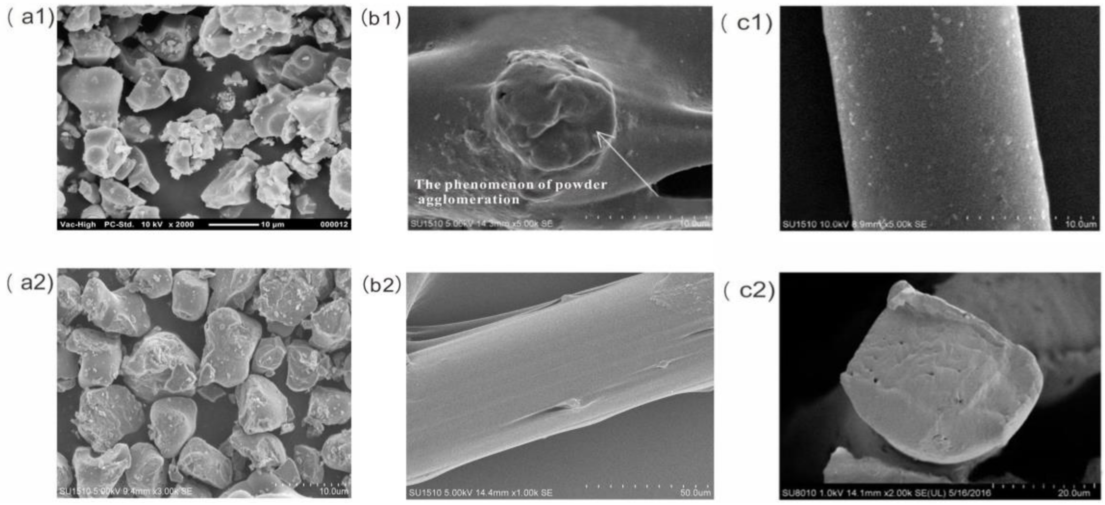


Fig. 1. SEM photographs: (a1) $SrAl_2O_4:Eu^{2+}$, Dy^{3+} powders; (a2) KH550 modified $SrAl_2O_4:Eu^{2+}$, Dy^{3+} ; (b1) Agglomeration phenomenon of powder in luminous fiber with unmodified phosphors; (b2) Surface morphologies of the luminous fiber doped with TSHF; (c1) Surface morphologies of the luminous fiber doped with modified phosphors; (c2) Cross-section diagram of luminous fiber doped with modified phosphors

The significant powder agglomeration can be observed in Fig. 1 (b1), since the luminous fiber was doped with unmodified phosphors, which indirectly affected the uniformity of spinning. The surface of the luminous fiber doped with TSHF was more smooth and without surface particles in Fig. 1 (b2). As shown in Fig. 1 (c1) and (c2), the surface of the luminous fiber doped with modified phosphors was dispersed more evenly than that in Fig. 1 (b1), exhibiting little agglomeration phenomenon, even thickness and diameter of about 20 microns.

3.2. Afterglow attenuation studies

Fig. 2 shows the afterglow decay curves of the luminous fibers. The decay trends of these samples were overall similar, but their initial afterglow intensities were somewhat different. The initial brightness showed an increasing trend as the amount of TSHF increased from 0 wt% to 0.5 wt%. However, the afterglow brightness of the fiber dramatically decreased when the mass ratio of TSHF exceeded 0.5%. The results from the above analysis indicated that TSHF doping affects the initial brightness of the fibers. Moreover, it is implied that excessive TSHF doping may result in the increase of doping concentration for raw material and readily lead to fluorescence quenching in the luminescence center of the fiber.

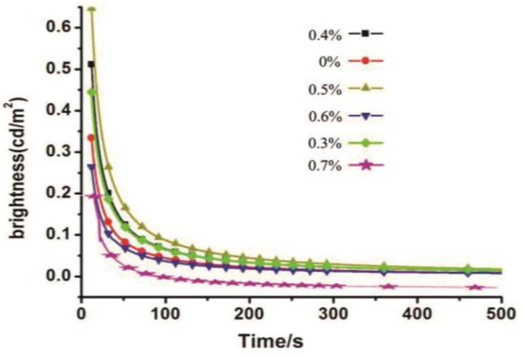


Fig. 2. Influence of TSHF on afterglow attenuation of the fiber (color online)

3.3. Photoluminescence studies

The emission spectra of the samples are shown in Fig. 3. As shown in Fig. 3 (a), the luminous fibers without TSHF doping emits at 520 nm under the excitation at 365 nm, corresponding to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} in the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} powder [15-17]. As shown in Fig. 3 (b), the fibers doped with TSHF exhibited dual-spectrum with two emission peaks in the range of 400-450 nm and near 520 nm, respectively. The blue emission peak at around 435 nm was attributed to the ultraviolet light absorption of TSHF, and the yellow-green emission peak at 520 nm resulted from the electron transfer of Eu^{2+} in the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} powder. With the increasing TSHF concentration, the emission wavelength of the peak at about 520 nm remained unchanged, but the relative intensity gradually decreased. Meanwhile, the intensity of the emission peak at about 400-450 nm gradually increased. Due to superposition of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} powder and TSHF spectra in the luminous fibers, when the mass ratio of TSHF exceeded 0.5%, the emission intensity decreased and the emission peaks started to shift toward shorter wavelengths.

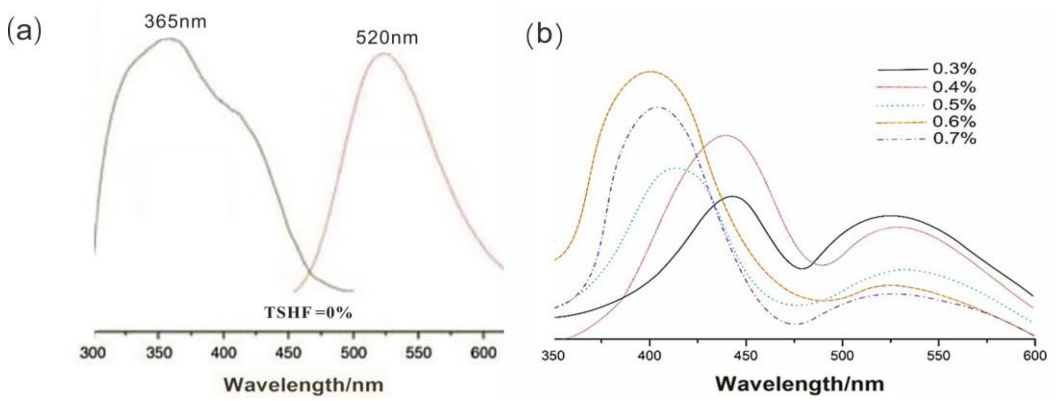
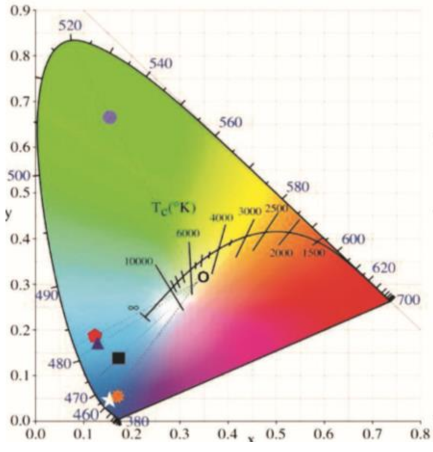
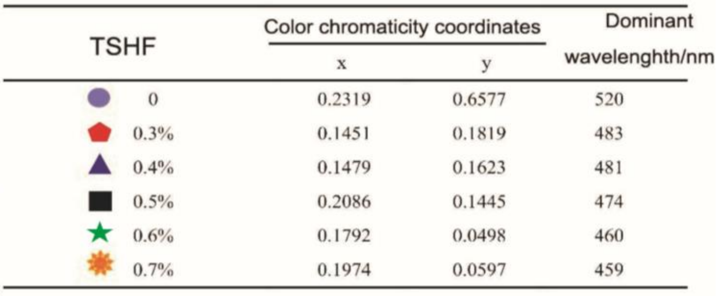


Fig. 3. Influence of TSHF on emission spectral characteristic of the fiber (Excitation spectrum at 365 nm): (a) Mass ratio of TSHF =0%; (b) Mass ratio of TSHF =(0.3% ~ 0.7%) (color online)





TSHF		Color chromaticity coordinates		Dominant wavelenghth/nm
		x	y	
●	0	0.2319	0.6577	520
⬟	0.3%	0.1451	0.1819	483
▲	0.4%	0.1479	0.1623	481
■	0.5%	0.2086	0.1445	474
★	0.6%	0.1792	0.0498	460
✹	0.7%	0.1974	0.0597	459

Fig. 4. Influence of TSHF on colorimetric characteristics property of the fiber (color online)

Fig. 4 illustrates the CIE 1931 chromaticity diagram and the relevant color parameters of the fibers. The emission color of the samples with TSHF mass ratios ranging from 0.3% to 0.7% were primarily distributed in the blue area, and the emission peaks were located at around 440 nm. However, the color of the luminous fiber without TSHF doping was located in the yellow-green area with the emission peak at about 520 nm. The dominant wavelengths of the samples gradually decreased as the amount of TSHF increased, and the emission color shifted gradually toward the blue region. Therefore, the findings indicated that TSHF doping was critically important for the blue-shift phenomenon.

3.4. Energy transfer process and principle analysis

Based on the above experimental results, it can be concluded that TSHF modulates the light conversion efficiency of the blue-color emitting luminous fibers and exhibits blue-shift effect on the emission spectra of luminous fibers. The blue-shift phenomenon is illustrated in Fig. 3 and Fig. 4. When the doping amount of TSHF exceeded 0.5 wt%, the emission peaks began to exhibit the blue-shift phenomenon, and the emitting wavelength shifted gradually toward the blue region as the amount of TSHF increased. However, the specific mechanisms underlying the luminescence and energy transfer processes from TSHF to $SrAl_2O_4:Eu^{2+}$, Dy^{3+} in the fiber require further research.

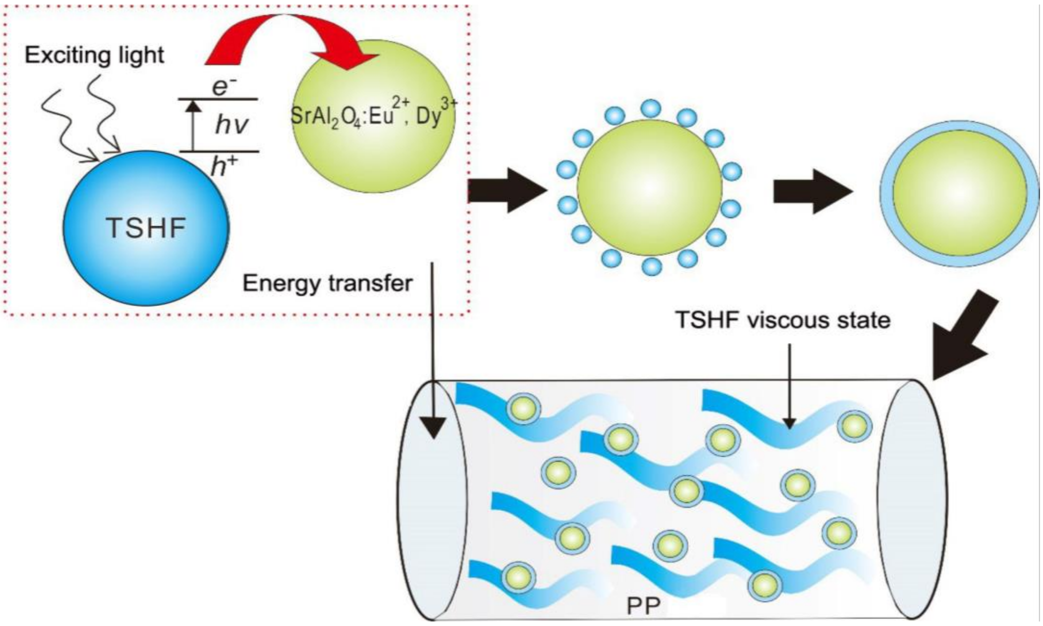


Fig. 5. Energy transfer schematic of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} powder and TSHF in the fiber (color online)

Fig. 5 is a schematic representation of energy transfer process in the fiber. With a conjugated system, TSHF can act as an energy donor, and its conjugated double-bond chromophores can absorb light and transition into an excited state. Subsequently, the molecules in the excited state can transfer excess energy to the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} acceptor in the fiber. The instantaneous luminescence of the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} in the rare earth aluminium strontium luminescent materials can accept energy from the conjugated polymer system, and enter the excited state while emitting the characteristic fluorescence of each ion [15-17]. In addition, an accompanying photochemical reaction between TSHF and $SrAl_2O_4:Eu^{2+}$, Dy^{3+} yields a diphenyl sulfide free radical ($Ar_2S^{+}\cdot$) and a reactive phenyl radical ($Ar\cdot$) [18]. The photochemical reaction is described as:

$$
\begin{aligned}
&Ar_3S^{+}\ X^{-} \longrightarrow Ar_2S^{\dot{+}} + Ar\cdot + X^{-} \\
&Ar_2S^{\dot{+}} + RH \longrightarrow Ar_2S^{+}\!-H + R\cdot \\
&Ar_2S^{+}\!-H \longrightarrow Ar_2S + H^{+}
\end{aligned}
\qquad (1)
$$

where Ar is the aryl group, X is SbF_6^-, RH is the monomer or prepolymer, and H+ represents the monomer or prepolymer.

Triarylsulfonium hexafluoroantimonate (TSHF) has a sensitizing effect in addition to its roles in photoinitiating polymerization. Since the main absorption of the photoinitiating material is insufficient, the photoinitiating property of the onium salt can be enhanced by adding a sensitizer to promote the phosphonium salt molecules to the excited state. In order to achieve the sensitization effect, it is necessary to integrate another fluorescent substance ($SrAl_2O_4$:Eu^{2+}, Dy^{3+}) with the photoinitiating material. The mechanism of sensitization is that TSHF can incorporate more photoenergy through energy transfer from another fluorescent donor molecule.

4. Conclusions

The above investigation of photoluminescence properties of the luminous polypropylene fiber with TSHF doping provides helpful insight into the blue-shift behavior of the emission spectra. TSHF was found to not only plays the role of adjusting the colors of the luminous fibers but also improves light conversion efficiency of the luminescent center. The outcomes of the investigation provide guidance for the development of blue-light emitting luminous polypropylene fiber. The main findings are outlined as follows:

(1) The SEM analysis showed that the surface properties of the fibers doped with modified $SrAl_2O_4$:Eu^{2+}, Dy^{3+} powders were markedly improved. After modification with KH550, the powders showed even thickness and absence of agglomeration phenomenon.

(2) TSHF doping affected the initial brightness of the fiber in a certain extent. The afterglow brightness of the fibers declined dramatically when the mass ratio of TSHF exceeded 0.5 wt%.

(3) The emission spectrum started to exhibit a blue-shift phenomenon when the mass ratio of TSHF exceeded 0.5%. Accordingly, the energy transfer from TSHF to $SrAl_2O_4$:Eu^{2+}, Dy^{3+} in the fiber reached optimal efficiency at the wavelength of 440 nm. The underlying mechanism of the blue-shift phenomenon described in this paper was that the TSHF can obtain additional photoenergy by receiving energy transfer from the $SrAl_2O_4$:Eu^{2+}, Dy^{3+} donor.

Acknowledgments

This study was financially supported by the National Natural Science Foundation of China (NO.51803096) and K.C. Wong Mangna Fund in Ningbo University.

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