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Study on the Photochromic Properties of Coloured Luminous Fibres Based on PA6

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Abstract
Coloured PA6 luminous fibres were prepared by adding luminous material and inorganic pigments. The morphology and optical properties of the coloured PA6 luminous fibres were characterized. The results revealed that luminous materials were dispersed uniformly in the fibres without obvious agglomerates. The yellow inorganic pigment and luminous material might induce a reduction in the PA 6 fibre crystallization degree. The luminous fibres emitted long-lasting phosphorescence with an excitation peak at 360 nm and emission peak at 515 nm. However, the excitation spectrum of the PA6-Y exhibited three peaks. The decay curves revealed that the yellow inorganic pigment enhanced the brightness of PA6 luminous fibres. The PA 6 luminous fibres had low colour purities and a high colour rendering index. There was no obvious difference among the emissive colours of the luminous fibres, and the colours of luminous fibres were similar to those of the pigments added.

Key words: *$SrAl_2O_4$, Eu^{2+}, Dy^{3+}, luminous fibre, luminescent property, colour characterization.*

Introduction

In recent years, the pollution of the environment and energy shortages have been attracting widespread interest. Environment protection and energy-saving are the main research content of the new century in different fields. Rare earth luminous fibres are produced with fibre-forming polymer and rare earth strontium aluminate luminous material. Strontium aluminate luminous material doped with rare soils is a new luminescent material developed since the 1990s, showing excellent properties such as high quantum efficiency, long lifetime and good stability [1 - 3]. Because of the addition of luminous material, the luminous fibres emit light without the necessity of any light source in the dark, which would play a warning and reminding role in the darkness. Luminous fibres are new functional textile material with no radioactivity, are safe for the human skin, and have broad prospects for application in many fields, including safety protective clothing, night work products, embroidery works and anti-counterfeiting products [4].

Researchers have long focused on the preparation of luminous fibres and luminous material [5 - 9], but the problems of colour monotony and lower afterglow brightness have also arisen. In recent years, considerable attention has been paid to research on the preparation of coloured luminous fibres with higher brightness. Some researchers developed coloured luminous fibres by adding inorganic pigments to spinning base material [10], but the photochromic properties of coloured luminous fibres were not studied in depth. In order to improve colour monotony and analyse the photochromic properties of coloured luminous fibres, coloured luminous fibres were produced based on PA6 with the addition of luminous material and three inorganic pigments of red, yellow and blue, respectively. We obtained four samples: white luminous fibre with no pigment, red luminous fibre, yellow luminous fibre and blue luminous, which were ordered as PA6-W, PA6-R, PA6-Y and PA6-B. The luminescence properties and colour performance of the products were investigated by spectra and chromaticity diagram measurement, and the relationship between the colour characterization and luminous property was discussed.

Experimental procedures

Materials

Such materials as $SrCO_3$ (A.R.), Al_2O_3 (A.R.), Eu_2O_3 (4N), Dy_2O_3 (4N) and H_3BO_3 (A.R.) were all purchased from Sinopharm Chemical Reagent Co, Ltd, and PA6 chips (super bright, melting point of 220.8 °C, opaque) were purchased from Wuxi Taiji Industry Co, Ltd. (Wuxi, China), while inorganic pigments and functional additives were supplied by Jiangsu Guoda Complete Wiring Equipment Co, Ltd (Wuxi, China). The inorganic pigments' characteristics are shown in ***Table 1***.

Synthesis of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors

$SrCO_3$, Al_2O_3, Eu_2O_3, Dy_2O_3 and H_3BO_3 were employed as raw materials, all of which were analytically pure.

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Table 1. *Inorganic pigment characteristics.*

Inorganic pigments	Chemical composition	Size, μm	Heat resistance, °C	Photostability	Weather resistance	Acid and alkali resistant
Cadmium red	Cd-Se-S	2.5	900	7	5	5
Nickel antimony titanium yellow	Ni/Sb/Ti		1000	8		
Cobalt blue	Co/Al					

The raw materials were weighed according to the nominal compositions of $SrAl_2O_4:Eu^{2+}$, Dy^{3+}. The powders were mixed and milled homogeneously for 2 h. The mixture powders were next calcined at 1200 °C for 3 h in an active carbon atmosphere to produce $SrAl_2O_4:Eu^{2+}$, Dy^{3+}, and then $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors for producing luminous fibres were obtained by grinding to the size of 7 - 8 μm.

Preparation of coloured PA 6 luminous fibres [10]

Coloured PA 6 luminous fibres were prepared with composite spinning equipment supplied by Jiangsu Guoda Complete Wiring Equipment Co, Ltd (Wuxi, China). The PA 6 chips were dried in an oven and then mixed uniformly with the above-obtained luminous material weighed at 5% [11] and inorganic pigments weighed at 10% [11] in a high-speed mixer. The mixtures were then extruded in a twin-screw master batch producer (screw diameter of the extruder - 65 mm and screw length-diameter ratio - 9) to get master batches for the spinning application. After drying for 20 h at 110 °C, the master batches were melted at 250 °C at a 3000 m/min winding speed and spun to produce coloured PA 6 luminous fibres. We got four samples: white PA 6 luminous fibre, red PA 6 luminous fibre, yellow PA 6 luminous fibre and blue PA 6 luminous fibre, which were named PA6-W, PA6-R, PA6-Y, and PA6-B, respectively.

Characterization

Preparation of measuring samples:

The measuring samples were luminous fibres fixed onto hard paper cards by the winding method. The dimensions of the paper cards were 6 cm by 10 cm, and the winding layer of the luminous fibres was greater than 10 to ensure the paper card was completely covered by luminous fibres.

The morphology of PA 6 luminous fibres was analyzed by Fei Quanta200 Scanning Electron Microscopy, made in Netherlands, after gold coating.

Structural analysis using XRD was performed on a Bruker AXS D8 Advance Diffractometer, made in Germany. Radiation was produced by a Cu X-ray tube at 40 kV, 40 mA with a 3° - 90° scan scope and 4°/min scan speed.

FT-IR spectra were recorded with a Nicolete is 10 FT-IR spectrometer, made in America, in the range of 400 - 4000 cm^{-1}.

Photoluminescence measurements were carried out with an F-4600 type fluorescence spectrophotometer, made in China, with a 150 W xenon lamp as the excitation source, at room temperature. The excitation and emission slit widths were both 5 nm with 380 V voltage, and the measuring photophysical parameters were consistent for all specimens.

Afterglow intensity profiles of the samples were obtained using a PR-305 Long rays fluorescence tester, made in China, with an excitation illumination of 1000 lx for 15 min. After stopping the excitation for 10 s, measuring was started for 3600 seconds and the time intervals were 1 seconds.

Colour characterization was carried out with a SPR-920 spectroradiometer, made in China, with a scan length from 380 to 780 nm and sampling interval of 5 nm.

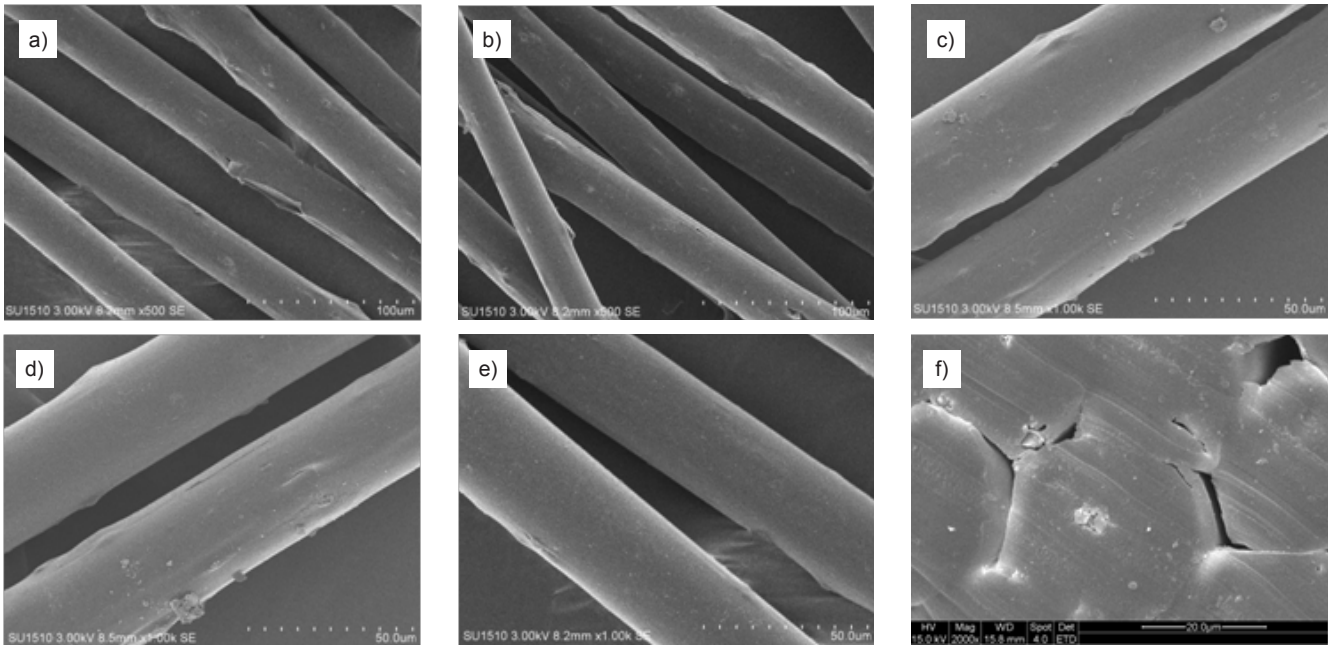

Figure 1. *SEM images of coloured PA 6 luminous fibres at different magnification; a) PA6-W 500×, b) PA6-B 500×, c) PA6-W 1000×, d) PA6-R 1000×, e) PA6-Y 1000×, f) PA6-W 2000×.*

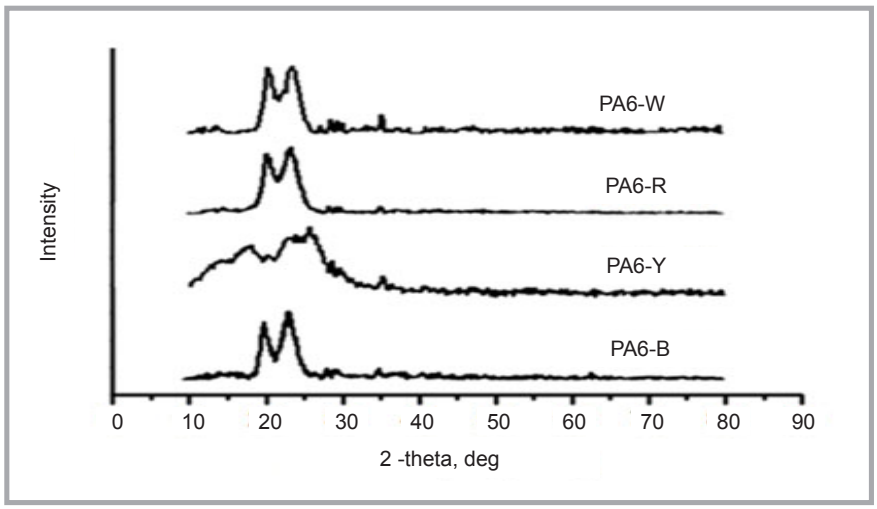

Figure 2. *XRD of coloured PA 6 luminous fibres.*

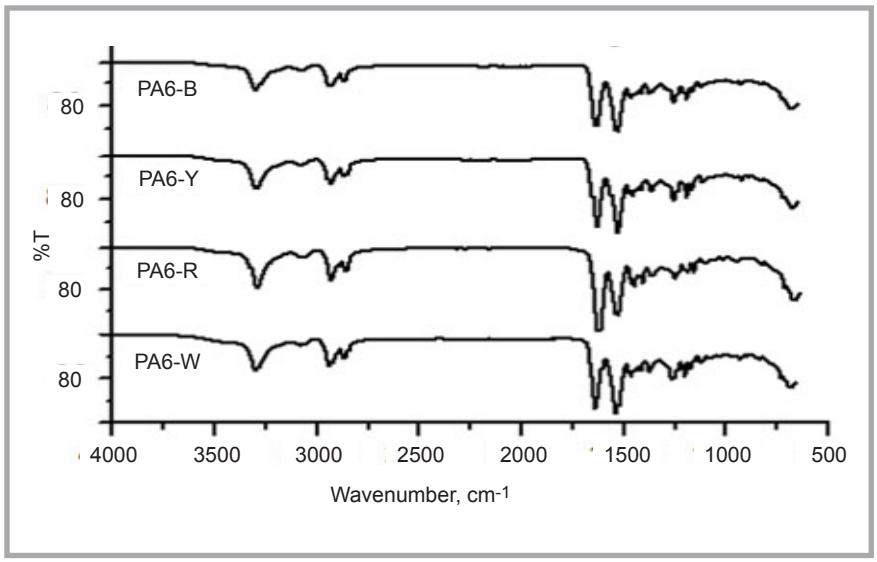

Figure 3. *FT-IR spectrum of coloured PA 6 luminous fibres.*

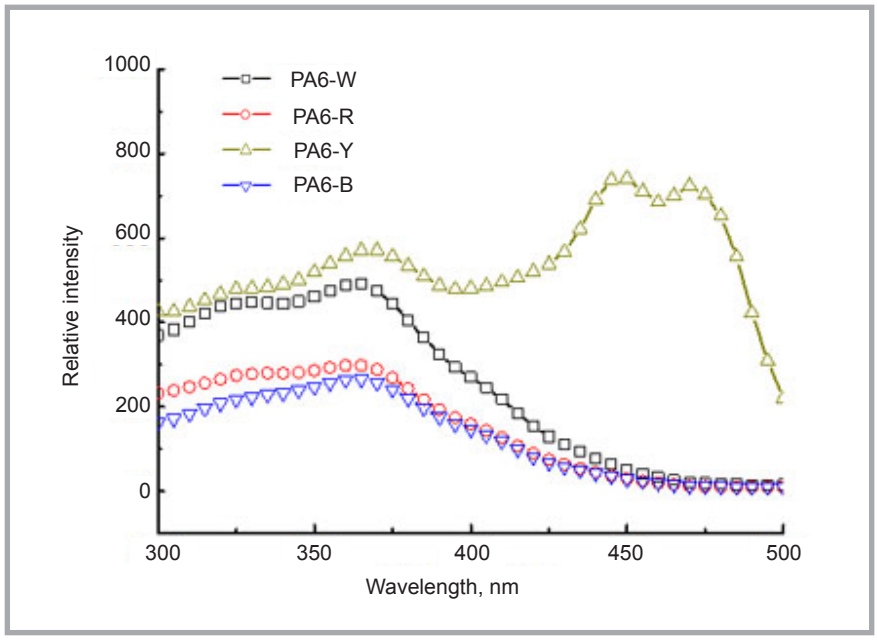

Figure 4. *Excitation spectrum of coloured PA 6 luminous fibres.*

Results and discussion

Morphology characteristic of PA 6 luminous fibres

By optimising the governing parameters, PA 6 luminous fibres were prepared by the melt spinning process [10]. The morphologies of PA 6 luminous fibres are shown in ***Figures 1.a*** PA6-W magnified 500×, ***1.b*** PA6-B magnified 500×, ***1.c*** PA6-W magnified 1000×, ***1.d*** is PA6-R magnified 1000×; ***1.e*** is PA6-Y magnified 1000×, and ***1.f*** PA6-W magnified 2000×. From ***Figure 1***, the PA 6 luminous fibres are uniform in diameter and spun yarn quality, and there is no difference between the modified fibres. Analysed from the manufacturing process of PA 6 luminous fibres, inorganic pigments and luminous materials are evenly dispersed in the fibre. The surfaces of the fibres are rough with small sprinkled particles, which might be caused by the rare-earth luminous materials being liable to escape from the surface of the fibres. As seen from ***Figure 1***, inorganic pigments could not affect luminescence material dispersion in the fibre, and luminous materials were dispersed uniformly on the fibre surface without the obvious agglomerates phenomenon.

XRD characteristic of PA 6 luminous fibres

The XRD spectrum of coloured PA 6 luminous fibres is given in ***Figure 2***. It shows that there are two strong diffraction peaks at 2θ = 20.3°, 23.6° and three weak peaks at 2θ = 28.6°, 30.2° & 35.6°, which illustrates that PA 6 luminous fibres have high crystallinity and retaine characteristic peaks of $SrAl_2O_4:Eu^{2+}$, Dy^{3+}. However, compared with the other three PA 6 luminous fibres, the diffraction of PA 6-Y luminous fibre reaches a peak at 2θ = 17.9°, 25.7° in the XRD graph and becomes inconspicuous, which indicates that the crystallization degree of PA 6-Y luminous fibre shows a decreasing tendency. This result might be due to the interaction of yellow inorganic pigments and luminous material, which influenced the crystallisation degree of PA 6-Y luminous fibre. In the spinning process, the addition of yellow inorganic pigments might have an effect on the crystallisation degree of $SrAl_2O_4:Eu^{2+}$, Dy^{3+}, which destroyed the regulation degree of the PA molecular chain structure. Therefore it is hard for PA molecular chains to crystallise with the crystallisation degree decreasing.

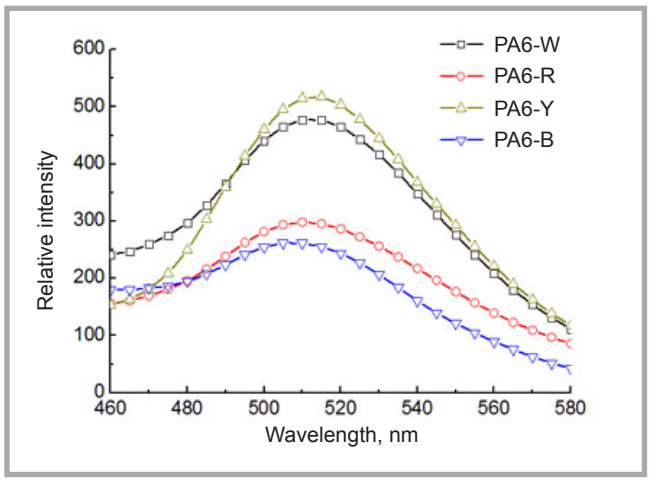

Figure 5. *Emission spectrum of coloured PA 6 luminous fibres.*

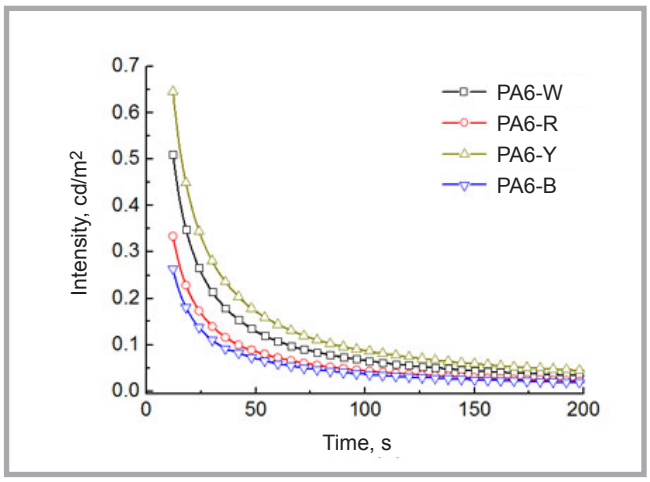

Figure 6. *Decay curves of coloured PA 6 luminous fibres.*

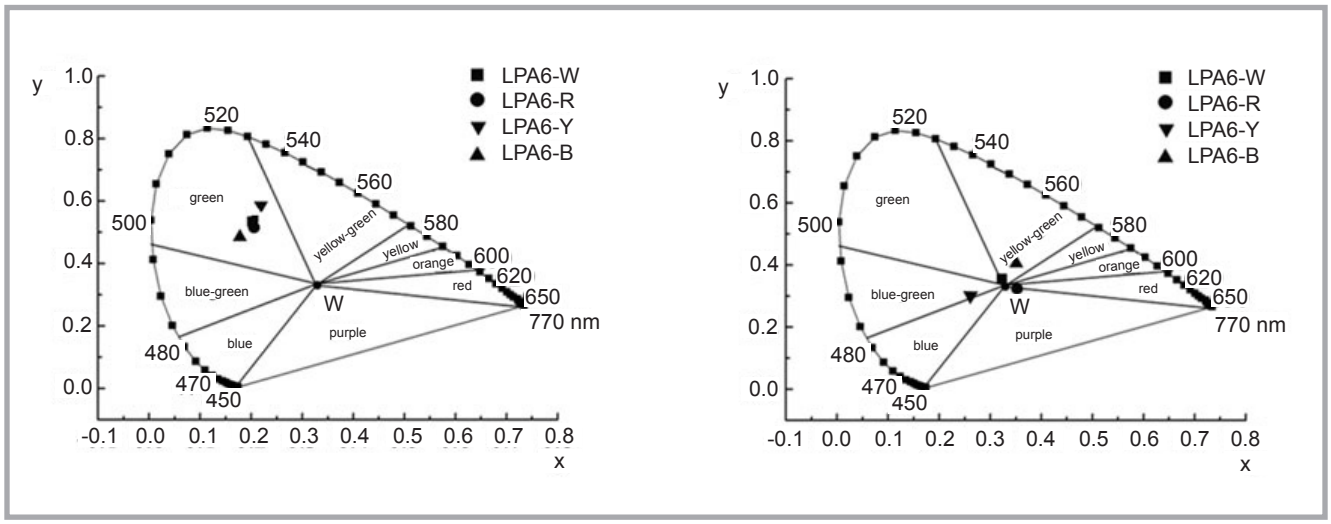

Figure 7. *CIE 1964 chromaticity diagram of coloured PA 6 luminous fibres.*

FT-IR characterization of PA 6 luminous fibres

The FT-IR spectrum of the PA 6 luminous fibres is shown in ***Figure 3***. The bands at wave number 3297 cm^{-1} correspond to N-H stretching vibration absorption and 1636 cm^{-1} to C=O stretching vibration absorption, being typical asymmetric vibration of the amide group. In addition, 2862 cm^{-1} corresponded to C-H stretching vibration absorption, 1199 cm^{-1} and 1260 cm^{-1} to C-N stretching vibration absorption, and 1533 cm^{-1} and 2945 cm^{-1} to N-H deformation vibration absorption. The FT-IR spectrum indicated that inorganic pigments and luminous materials had little impact on macromolecular structure of PA 6 luminous fibre. However, a weak band at about 520 cm^{-1} corresponding to the stretching vibration of Eu–O [12] can be observed in the ligands, which indicates that the coordination bonds between Eu^{2+} ion and PA 6 could be formed in the complex.

Luminescent properties of PA 6 luminous fibres

Excitation spectrum and emission spectrum of PA 6 luminous fibres

Figure 4 shows the excitation spectra of PA 6 luminous fibres at room temperature with an emission wavelength of 520 nm. The excitation spectra of the four samples show a broad band from 300 to 500 nm with a peak around 360 nm, which is the same as that of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphor [13]. The whole range of excitation spectra is located at the ultraviolet light border with visible light, with ultraviolet light having a comparative advantage in excitation power. However, the excitation spectrum of the PA6-Y exhibits a hump characteristic curve with three peaks at around 360, 450 and 470 nm, respectively. Comparing with the other three excitation spectra, the excitation spectrum of sample PA6-Y blue obviously shift and all split into two components, which might be attributed to the fact that the addition of yellow inorganic pigments affects the crystalline structure and trap level of the luminous material. It is concluded that visible light can readily excite the luminous fibres, and different excitation light sources can excite differently coloured luminous fibres in various degrees.

Figure 5 shows the emission spectra of the PA 6 luminous fibres at an excitation wavelength of 360 nm. As seen from ***Figure 5***, the emission spectrum profiles of the four samples are in the regions of 450 - 600 nm, with the peak at around 515 nm, which are slighted shorter than the 520 nm of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} powder prepared by the usual solid state reaction method [14, 15]. PA6-Y has the highest brightness, followed by PA6-W, PA6-R and PA6-B. From the analysis above, we can state that the addition of yellow inorganic pigment enhanced the brightness intensity of PA6 luminous fibre,

Table 2. Emissive colour characteristics of luminous fibres.

Samples	Chromaticity coordinates		Domain. w	Purity	Ra
	x	y			
LPA6-W	0.3461	0.5231	558	0.656	90.5
LPA6-R	0.4285	0.3946	583	0.525	93.6
LPA6-Y	0.4084	0.4533	572	0.631	89.6
LPA6-B,	0.4340	0.4106	581	0.584	91.3

Table 3. Colour characteristics of luminous fibres.

Samples	Chromaticity coordinates		Domain. w
	x	y	
LPA6-W	0.3234	0.3456	539
LPA6-R	0.3468	0.3169	685
LPA6-Y	0.3426	0.3895	562
LPA6-B	0.2631	0.2971	484

and the other two inorganic pigments weakened its brightness intensity. There was only a small difference between the emission spectra of PA6-W and PA6-Y fibres. From the luminescent process of luminous fibres, when the excited light entered the fibre and propagated within it, the track of excited photons in the fibre was affected by the luminous materials and coloured pigments to produce differently coloured emission light, which determined the emission colours of luminous fibres. The smaller the colour difference between the luminous materials and coloured pigments, the less the effect of coloured pigments on the luminescent properties of the luminous materials and fibres. The colour of yellow pigment was close to that of the luminous materials, which resulted in a small difference between the emission spectra of PA6-W and PA6-Y fibres.

Afterglow decay curve of PA 6 luminous fibre

Figure 6 shows the decay curves of PA 6 luminous fibres measured at room temperature. As shown in ***Figure 6***, the initial brightness and decay speed of long afterglow phosphor are different from each other. The initial brightness of PA6-W, PA6-R, LPA 6-Y, and PA6-B is 511, 334, 647 & 263 mcd/m^2, respectively. Compared with the other three samples, PA 6-Y has a higher initial brightness. Therefore PA 6-Y has better long –lasting phosphorescence. The poor long –lasting phosphorescence of PA6-R, and PA6-B could be due to the addition of inorganic pigments, which would weaken the brightness of the luminous material. PA 6-Y has longer – lasting phosphorescence than the others because of the addition of yellow inorganic pigments, which might have an effect on defects of the luminescent center, and the defect levels of the luminous powder.

Chromatic characterisation of PA 6 luminous fibre

Featured parameters of the emissive colour and colour of PA 6 luminous fibres are shown in ***Tables 1*** and ***2***, respectively. It can be seen from ***Table 1*** that the dominant wavelengths of emissive colour among PA 6 luminous fibres show a small difference from 558 to 583 nm, and the dominant wavelengths of PA 6-W emissive colour prepared without mixing any inorganic pigments is are observed at 558 nm, which is similar to those of the luminescence material at 548 nm. From ***Table 2***, it can be seen that the dominant wavelengths of colour among PA 6 luminous fibres show a big difference from 484 to 685 nm, and only the dominant wavelengths of the PA 6-W colour are similar to those of the PA 6-W emissive colour.

From ***Table 1*** it can be seen that the colour purities of PA 6 luminous fibres are similar and not suitable. The reason is that the emission spectra of PA 6 luminous fibres are in a broad band containing light of yellow, green and blue which are mixed to become yellow-green light. Therefore, the emitting colours of PA 6 luminous fibres are not monochromatic lights. The best colour purity of the samples is possessed by PA 6-W, whose colour purity is 0.656, and the worst by PA 6-R, with a colour purity of 0.525.

As a new kind of functional fibre, PA 6 luminous fibres could send out colour light by itself in darkness, and can be regarded as a light source. The colour render index (CRI) is an important index of light sources for evaluating luminescent properties, describing the colour difference of objects under a studied light source as well as standard light sources expressed in Ra in the range from 0 to 100. When the Ra is 100, the colour of the objects under the studied light source consists of that under a standard light source. The spectral distribution of the light source is closely related to the colour render index property. The emission spectra of PA 6 luminous fibres are a high-brightness light series which have a continuous spectrum similar to that of sunlight and a fluorescent lamp with a high colour rendering index. It can be seen from ***Table 1*** that, except PA 6-Y luminous fibre with Ra 89.6, the colour rendering indexes of the other four PA 6 luminous fibres are satisfactory up to a value of 90, achieving an excellent level. As shown in ***Figure 7***, the light colours of the PA 6 luminous fibres are mostly located in the yellow-green areas, in which the human eyes have greater sensitivity. Therefore the PA 6 luminous fibres could be easily identified in the darkness.

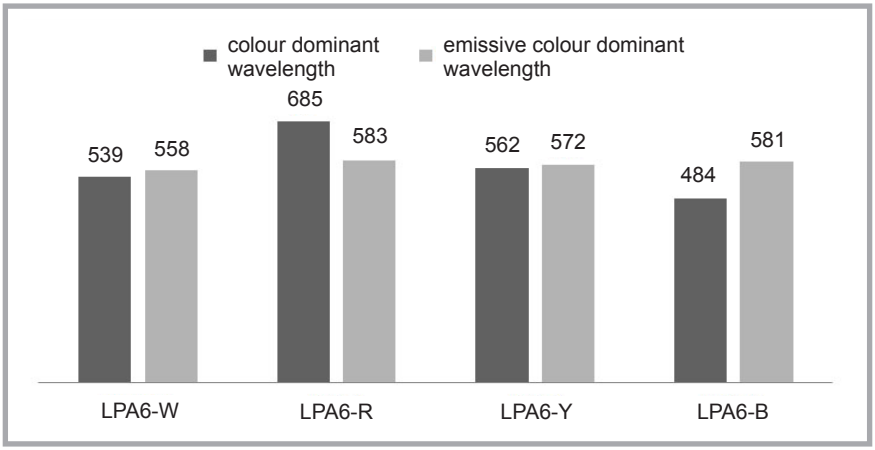

Figure 8. *Dominant wavelength of the emissive colour and colour of luminous fibres.*

According to the X and Y values in ***Tables 1*** and ***2***, the positions of the five samples are identified in the CIE 1964 chromaticity diagram shown in ***Figures 7.a*** the emissive colour chromaticity diagram in CIE 1964, and ***7.b*** the colour chromaticity diagram in CIE 1964. According to the dominant wavelength values in ***Tables 1*** and ***2***, the difference in the dominant wavelength of the emissive colour and colour is shown in ***Figure 8***. As shown in ***Figure 7.a***, the emissive colours of the luminous fibres are mostly located in the green areas, which shows the similarity of the dominant wavelengths of the samples' emissive colours and consistency with the dominant wavelengths tested in ***Table 2.*** From ***Figure 7.b***, the colours of the luminous fibres are located in different areas, and those of PA6-W, PA6-R, PA6-Y and PA6-B are white, red, yellow and blue, which is consistent with the dominant wavelengths tested in ***Table 3***. The similarity between emissive colours and the differences between colours can be clearly obtained from ***Figure 8***. From what has been discussed above, we can arrive at the conclusion that the addition of inorganic pigments had certain effects on the dominant wavelengths of the coloured luminous fibres, but failed to change the colour of the emission lights, which was still a visible green light similar to the emission light colour of the luminous material.

Conclusions

The long afterglow profile of luminescence material $SrAl_2O_4$:Eu^{2+}, Dy^{3+} was synthesised by the solid-state reaction method, and coloured luminous fibres were prepared by the melt spinning process based on PA6. The surface morphologies, crystal characteristic, structure, luminescent properties and chromatic characterisation of coloured PA 6 luminous fibres were investigated. The SEM photographs indicated that inorganic pigments and luminous materials were mixed evenly with Polyamide 6, and luminous materials were dispersed uniformly in the fibre surface without the obvious agglomerates phenomenon. With the XRD data obtained, the crystallisation degrees of PA 6 luminous fibres were reduced because of the addition of inorganic pigments and luminous materials. The FT-IR spectrum indicated that inorganic pigments and luminous materials had little impact on the macromolecular structures of PA 6 luminous fibre; however, the coordination bonds between the Eu^{2+} ion and PA 6 could be formed in the complex. After being irradiated with ultraviolet light, PA 6 luminous fibres emitted long lasting yellow-green phosphorescence, with an excitation peak at 360 nm and emission peak at 515 nm. However, the excitation spectrum of PA6-Y exhibits a hump characteristic curve, with three peaks at around 360, 450 and 470 nm, respectively. According to the PL spectra and the luminance decay curves, the red and blue inorganic pigment weakened the brightness intensity of PA6 luminous fibre. On the other hand, the yellow inorganic pigment enhanced the brightness intensity. Under the coloured pigment's influence, there was a certain deviation in the colour and emissive colour of luminous fibres, which affected human visual perception and feelings. The PA6 luminous fibres had low colour purities and a satisfactory colour render index. There was no obvious difference among the emissive colours of luminous fibres nor among the colours of luminous fibres because of pigment addition.

The interactions of yellow pigment with the PA6 chain have been not confirmed by FTIR analysis. Recently I have been working in order to describe the interaction between the composition of yellow pigment and functional groups of PA6, but that basic reason has not been established yet. This problem is the main objective of my future study.

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