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Preparation and luminescence studies of thermosensitive PAN luminous fiber based on the heat sensitive rose red TF-R1 thermochromic pigment

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ABSTRACT

The aim of this study was to prepare and demonstrate a new kind of thermosensitive luminous fiber based on optical interference of thermochromic pigments. The surface morphology of a thermosensitive luminous fiber, containing $Sr_2ZnSi_2O_7$: Eu^{2+}, Dy^{3+}; Y_2O_2S: Eu^{3+}, Mg^{2+}, Ti^{4+}; and heat-sensitive rose red TF-R1 thermochromic pigment, was analyzed by scanning electron microscope (SEM). The X-Ray Diffraction (XRD) results revealed the crystal structure of the fiber samples and the synthesized rare-earth luminescence materials. There was no degradation of the crystalline phases in the blend when blending and spinning. The thermodynamic stability and dynamic phase structure were analyzed by Thermal Gravity Analysis (TGA) and Differential Scanning Calorimetry (DSC). This thermosensitive polyacrylonitrile (PAN) luminous fiber was stable below 200 °C. The fluorescence spectra, reflectivity spectra were measured to reveal the phosphorescence and thermochromism, and visual testing was also performed. The phosphorescence colors of the thermosensitive luminous fiber were directly related to the temperature. The prepared fiber samples had a red emission at room temperature, and because of the inner phase transition of the heat-sensitive rose red TF-R1 thermochromic pigment on heating, the fiber samples became colorless with blue light emission. This novel thermosensitive luminous fiber has many potential applications in optical and thermal sensors.

1. Introduction

Luminous fiber is a very promising new functional material because of its high brightness, long afterglow time, and stability. In the decade since luminous fiber was first introduced to the public, it has attracted a large amount of research interest, and the technology has progressed substantially. Luminous fibers with $SrAl_2O_4$: Eu^{2+}, Dy^{3+}, $Sr_2ZnSi_2O_7$: Eu^{2+}, Dy^{3+} and Y_2O_2S: Eu^{3+}, Mg^{2+}, Ti^{4+} blending have been successfully fabricated in polyethylene terephthalate, polypropylene, and polyamide to prepare luminous fiber with various light-emitting spectral characteristics [1–4]. For example, $SrAl_2O_4$: Eu^{2+}, Dy^{3+} luminous fiber has been developed for commercial purposes. Attempts have been made to blend binary or ternary long-lasting luminous materials with fiber-forming polymers to analyze the possibilities of polychromatic light-emitting luminous fiber [5,6]. Polychromatic luminous fiber is the significant precursor that laid the foundation for the invention of thermosensitive luminous fiber. Polyacrylonitrile (PAN) is a widely used fiber-forming polymer in the textile and carbon-fiber industries. At present, it is possible to prepare commercial PAN fiber via wet spinning or gel spinning because of the structural characteristics of PAN [7]. Some organic solvents such as dimethylsulfoxide (DMSO), dimethylformamide(DMF), etc. have been used to prepare spinning solutions [8]. Based on the additive three primaries, $Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+} with blue light emission and Y_2O_2S: Eu^{3+}, Mg^{2+}, Ti^{4+} with red light emission, binary-blended PAN luminous fiber has polychromatic light-emitting behavior. Depending on the ratio of $Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+} to Y_2O_2S: Eu^{3+}, Mg^{2+}, Ti^{4+}, binary-blended PAN luminous fiber could emit blue, red, purple, or magenta light [9].

The fluorane derivative, consisting of spiro-isobenzofuran and a chromophore, is an important leuco dye. The heat-sensitive rose

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red TF-R1 is a typical fluorane derivative that has lignocaine as the chromophore with a red color. Moreover, because of the benzofluorane, which extends the conjugated system, the substituent with large conjugation will lead to a red shift [10–14]. Because of the above properties, the heat-sensitive rose red TF-R1 has been widely used in reversible thermosensitive materials. Based on the formation or destruction of the ternary compound among the leuco dye, developer, and co-solvent driven by interactions in the solvent, the temperature of the thermochromic behavior is influenced by the melting temperature of the co-solvent [15–19]. The thermochromic equation can be seen in Fig. 1 (the co-solvent is the tetradecanol).

In this study, the PAN was employed as the fiber-forming matrix. $Sr_2ZnSi_2O_7$: Eu^{2+}, Dy^{3+}; Y_2O_2S: Eu^{3+}, Mg^{2+}, Ti^{4+}; and a thermochromic pigment comprising the heat-sensitive rose red TF-R1, bisphenol A, and tetradecanol were blended in the PAN spinning solution via solution mixing. The spinning solution was well dispersed, and then spun into thermosensitive PAN luminous fibers [20–25]. Fig. 2 shows the process of light color change. A red filter membrane would be formed in the interior of binary-blended luminous fiber by blending in thermochromic pigment. On the macroscopic level, the thermosensitive luminous fiber presents red and has red light-emitting behavior. Rising temperatures encourage co-solvent fusion, and the heat-sensitive rose red TF-R1 will convert to a closed-ring structure and become colorless [26–29]. Thereupon, the barrier that blocks blue light disappears. The blue light can be easily seen with the naked eye when the fiber becomes colorless.

2. Experimental details

2.1. The raw materials

$SrCO_3$, ZnO, SiO_2, Eu_2O_3, Dy_2O_3, H_3BO_3, Y_2O_3, S, TiO_2, $4MgCO_3 \cdot Mg(OH)_2 \cdot 6H_2O$, Na_2CO_3 of analytical reagent grade as the starting materials were purchased from Sinopharm Chemical Reagent Co., Ltd., China. The polyacrylonitrile(PAN) powder were produced by the Shaoxing Gimel Advanced Materials Technology Co., Ltd. The dimethyl sulfoxide(DMSO) of analytical reagent grade as the spinning solvent was supplied by Sinopharm Chemical Reagent Co., Ltd., China. The commercial heat sensitive rose red TF-R1 pigment (the theoretical thermochromism temperature is 38 °C) was purchased from Shenzhen Bianse Science and Technology Co., Ltd.

2.2. Preparation of rare earth luminescent materials

$Sr_{1.95}ZnSi_2O_7$: $Eu^{2+}{}_{0.02}$, $Dy^{3+}{}_{0.03}$ and Y_2O_2S: $Eu^{3+}{}_{0.04}$, $Mg^{2+}{}_{0.05}$, $Ti^{4+}{}_{0.05}$ were synthesized using high temperature solid state method. After preliminary milling, these raw materials were respectively dissolved in appropriate amounts of absolute ethanol, followed by ultrasonic dispersion for 30min and mechanical mixing for 30min in order to get the homogeneous mixture. The samples were heated by adding flux (the ratio of H_3BO_3 to $Sr_{1.95}ZnSi_2O_7$: $Eu^{2+}{}_{0.02}$, $Dy^{3+}{}_{0.03}$ is 10 mol.%; the ratio of Na_2CO_3 to Y_2O_2S: $Eu^{3+}{}_{0.04}$, $Mg^{2+}{}_{0.05}$, $Ti^{4+}{}_{0.05}$ is 20mol.%) to a high temperature of 1300 °C for 3 h in a reducing atmosphere. The sintered products were re-milled in ball mill and sieved with 600 mesh to get the desired size.

2.3. Preparation of PAN thermosensitive luminous fiber

The rare earth luminous materials and the thermochromic pigment were added in homogeneous PAN/DMSO solution as the spinning dope(PAN/DMSO is 20% at mass-volume concentration). The thermochromic pigment was added in the PAN/DMSO spinning dope by the mass ratios of 10% and 15% to PAN. The prepared $Sr_2ZnSi_2O_7$: Eu^{2+}, Dy^{3+} (the mass ratio was 4% to PAN)and Y_2O_2S: Eu^{3+}, Mg^{2+}, Ti^{4+} (the mass ratio was 6% to PAN)were uniformly mixed in spinning dope. Wet spinning was carried out using the syringe and a boost device. The preparatory dope solution was spun into coagulation bath (deionized water) at room temperature(25 °C) with the push speed of 6 mL/min. The preparation process of thermosensitive luminous fiber process was given in Fig. 3.

2.4. Instrumental measurements

The surface morphologies of luminous fiber were characterized on Hitachi TM3030 scanning electron microscopy. The conventional fluorescence spectra and the luminescence color of thermosensitive luminous fibers were obtained at 25 °C, 35 °C and 45 °C with an excitation wavelength of 360 nm using the fluorescence spectrophotometer (FS5 Fluorescence spectrometer produced by Edinburgh Instruments) with the Xe flash lamp as an excitation source; the slit was 2 nm in width; the excitation wavelength was from 400 to 700 nm and the dwell time was 0.2s; chromaticity coordinates and reflectivity were tested using Macbeth color-Eye 7000A color measuring and matching

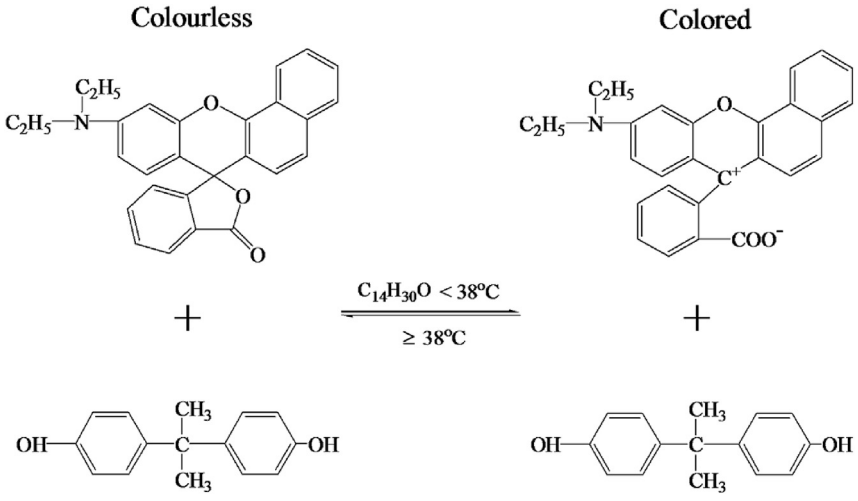

Fig. 1. The thermochromic process of reversible color change compound.