

## Development and characterization of the amidoxime/Europium (III)-chelated complex fibers

C. G. Hu<sup>1</sup>, S. L. Wang<sup>2</sup>, Z. Z. Wu<sup>1</sup>,  
Z. Zao<sup>3</sup>, G. Li<sup>4,5</sup>

<sup>1</sup> College of Textile and Clothing Anhui Polytechnic University, Wuhu 241000, P.R.China  
e-mail: huchenggong2014@163.com

<sup>2</sup> Anhui Business College of Vocational Technology, Wuhu 241000, P.R.China  
e-mail: wangsunlin2014@163.com

<sup>3</sup> State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P.R. China  
e-mail: tc ligang@suda.edu.cn

<sup>4</sup> National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, Suzhou 215123, P.R.China

<sup>5</sup> Nantong Textile Institute, Soochow University, Nantong, People's Republic of China

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### ABSTRACT

This paper presents a study of the amidoxime/Europium (III)-chelated complex (AECC) fibers which can be used as functional fibers for technical textiles such as decorations, protections and medical textiles etc. First, the  $\text{EuCl}_3$  solution were prepared and reacted with amidoxime fibers using optimized process conditions at 50 °C, 5 hours. Subsequently, the morphology, element analysis, fluorescence and mechanical properties of the AECC fibers were systematically investigated. Finally, the effects of different pH values and temperature on the content of Eu (III) complexes fiber were studied, respectively. The results showed that the AECC fibers possess enhanced fluorescence intensity and good mechanical properties. The results also illustrated that coordination reaction was identified between Eu (III) ions and amidoxime fiber and the electronic energy of C1s, O1s, N1s and Eu (III) ions in amidoxime fibers has significant changes compared to original fibers. The fluorescence emission bands of the AECC fibers were observed when the excitation wavelength  $\lambda$  equal to 380 nm. In conclusion, this study provided a theoretical basis for the preparation and practical application of fluorescent fibers.

**Keywords:** Amidoxime/Europium (III)-chelated, complex fibers, fluorescence, mechanical properties.

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### 1. INTRODUCTION

The rare earth luminous fiber has been increasingly used as functional fibers for technical textiles such as decorations, protections and medical textiles etc. The rare earth ions such as Sm (III), Eu (III), Tb (III), Dy (III) possess good fluorescence properties due to their special structural characteristics [1-4]. Chelating the amidoxime fibers with rare earth ions can produce amidoxime/Europium (III)-chelated complex (AECC) fibers which have excellent light-emitting intensity, good mechanical properties, and can free from harmful radiation [5,6]. They can absorb ultraviolet or visible light for ten minutes, and then can emit light continually for more than ten hours after removal of excitation resource [7, 8]. Such functional fibers can be used for technical textiles such as decorations, protections and medical textiles etc [5, 9-11]. However, few studies have been found about using chelating reaction method to fabricate AECC fibers.

The objective of this paper is to develop amidoxime/Europium (III)-chelated complex (AECC) fibers which have enhanced fluorescence intensity and good mechanical properties. First, the  $\text{EuCl}_3$  solution were prepared and reacted with amidoxime fibers using optimized process conditions. The amidoxime fibers were made from polyacrylonitrile (PAN) polymer which can be used in many applications such as electrospinning

fibers, carbon fibers and films due to its good anti-oxidant and chemical stability [12,13,14]. Subsequently, the morphology, element analysis, fluorescence and mechanical properties of the AECC fibers were systematically investigated. Finally, the effects of different pH values and temperature on the content of Eu (III) complexes fiber were studied, respectively.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Polyacrylonitrile (PAN) fiber was purchased from Anqing Petrochemical Plant; the water used for testing is deionized water; the amidoxime fiber was prepared using the previous method [15];  $\text{Eu}_2\text{O}_3$ , Hydroxylamine hydrochloride Sodium, Ethylenediaminetetraacetic acid disodium salt, Calcium carbonate and other reagents were of analytical grade.

### 2.2 Preparation of Amidoxime/Europium (III)-chelated complexes fiber

Adding 0.5030 g of  $\text{Eu}_2\text{O}_3$  weight by analytical balance into a clean, dry small beaker, and dissolved into 15 ml of concentrated hydrochloric acid, then heating by water bath until the solution was transparent and  $\text{Eu}_2\text{O}_3$  was completely dissolved. Stop heating until white crystals appear, remove the beaker and cool it at room temperature. Then dissolve the crystals in distilled water, and transfer it into 250 ml volumetric flask to constant volume and europium chloride solution was obtained.

Weighting above 1.0 g amidoxime fiber into a 100ml of  $\text{EuCl}_3$  solution with certain concentration and adjust the pH value of the solution, place it into a pot with a constant temperature water bath of 50 °C. After reacting about 5 hours, AECC fibers were prepared and then washed using 90 ml of deionized water for 10 times. The lotion and the rare earth ions solution after coordination reaction were blended together and then transferred into a 1000 ml of volumetric flask. Then determinate the concentrations of Eu (III) solution with method of complex metric titration, and calculate the content (T) of Eu (III) in AECC fibers using Equation (1). Choosing different pH values can obtain different AECC fibers with different colors.

$$T = (C_0V_0 - C_1V_1) \times M/m \text{ (mg/g)} \quad (1)$$

Where:  $C_0$  is the concentration of Eu (III) solution before reaction (mmol/L);  $V_0$  represents the volume of Eu (III) solution before reaction,  $V_0 = 0.1 \text{ L}$ ;  $C_1$  is the concentration of Eu (III) solution after reaction (mmol/L);  $V_1$  represents the molecular weight of Eu (III) at 151.965 g/mol; m is PAN mass (g).

### 2.3 Characterization of fluorescence and mechanical properties

The fluorescence spectra of AECC fibers were measured using HITACHIF-4500 fluorescence spectrometer. The tensile properties of AECC fibers were tested using LLY-068 electronic single fiber strength tester. The breaking strength and elongation at break of the fibers were repeated for 50 times by electronic single fiber strength tester and all data sets were expressed in terms of their mean and standard deviation.

### 2.4 X-ray photoelectron spectroscopy

The samples were characterized with an X-ray photoelectron spectroscopy (XPS) (Escalab MKII, British, Vacuum Generator Co., Ltd.). Analyses were performed on a surface analysis system with a MgK X-ray source, vacuum rate  $1.33 \times 10^{-7} \text{ Pa}$ , 10 scans. Samples were attached to the aluminum sample platform with double-sided tapes. Quantitative analyses were performed using peak areas and elemental sensitivity factors. Mean values were gotten from five different areas on one sample.

## 3. RESULTS AND DISCUSSION

### 3.1 Effects of different pH on Eu (III) content in AECC fibers

The original color of amidoxime fibers is white. When the value of pH was 1.0, the color of the fibers did not change significantly. As the pH value increased, the color of fiber gradually deepened, while the value of pH was above 5.0, the fiber color faded.

As shown in Table 1, when pH was equal to 1.0, the fiber was white. Because of the high acidity, the

groups of amidoxime fiber -NH<sub>2</sub> and -OH changed to be -ÑH<sub>3</sub> and -OH<sub>2</sub> respectively, and lost the ability to be coordinated reaction with Eu (III). The color of fiber deepened as the acidity decreased at pH < 3, and it showed that the content of Eu (III) in the fiber increased. The color of fiber faded as the acidity decreased and the content of Eu (III) in the fiber significantly reduced while pH > 4. The color of fiber was the darkest when pH = 3.0. Meanwhile, the content of Eu (III) in the fiber also reached the highest, and the amidoxime groups and Eu (III) were matched into stable mating structure.

**Table 1:** Effect of pH value of reaction system on the color of fiber and Eu (III) content

PH VALUE	COLOR OF FIBER	EU (III) CONTENT T	UNIT
1.0	White	0	(mg/g)
2.0	yellow-green (Deep)	94.90 ± 0.05	(mg/g)
3.0	yellow-green (Light)	40.56 ± 0.03	(mg/g)
4.0	yellow-green (Deep)	72.57 ± 0.14	(mg/g)
5.0	yellow-green (Light)	50.59 ± 0.03	(mg/g)

### 3.2 Effects of different temperature on Eu (III) content in AECC fibers

After blending 0.2 g amidoxime fibers with 25 ml Eu (III) solution in five erlenmeyer flasks, the pH of the solution was adjusted to 3.0, and then were placed at 20 °C, 25 °C, 35 °C, 45 °C and 55 °C to reaction for 5 hours, respectively. Finally, the fibers were removed and washed using deionized water. So different content AECC fibers were obtained. The Eu (III) content in AECC fibers under different reaction temperatures was calculated using Equation (1). The calculated results are given in Table 2.

**Table 2:** Effect of the reaction temperature on the color of fiber and the content of Eu (III) fiber

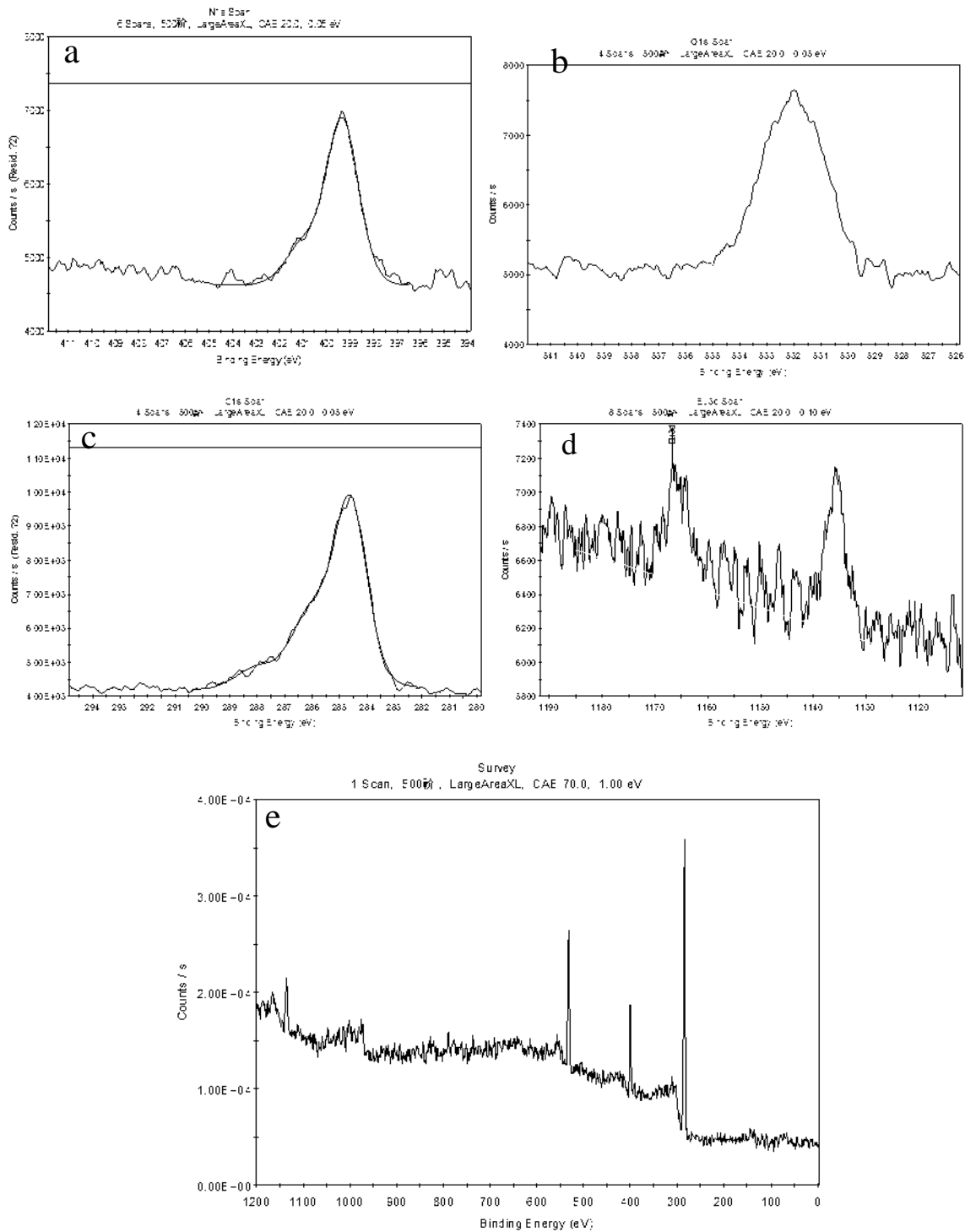
REACTION TEMPERATURE	COLOR OF FIBER	EU (III) CONTENT	UNIT
20 °C	Light yellow	5.65 ± 0.02	(mg/g)
25 °C	Light yellow	6.67 ± 0.03	(mg/g)
35 °C	yellow-green (Light)	23.55 ± 0.05	(mg/g)
45 °C	yellow-green (Deep)	90.69 ± 0.05	(mg/g)
55 °C	yellow-green (Light)	60.95 ± 0.04	(mg/g)

Temperature was an important factor affecting the reaction rate of PAN fibers and Eu (III) ion. Generally, the reaction rate increased as the increasing of temperature. As the data given in Table 1, the content of Eu (III) in AECC fibers increased significantly while the temperature changed to 35 °C, and the color deepened obviously. Little change of the content was observed at the lower temperatures. When the measured temperature was reached at 45 °C, the Eu (III) content in AECC fibers reached at maximum. While the measured temperature was increased to 55 °C, the Eu (III) content in the fibers decreased rapidly. Meanwhile, the color of fiber became lighter. Thus, the high temperature could destroy the structure of the fiber and decrease the mechanical properties.

### 3.3 XPS analysis of AECC fibers

As the data given in Table 3, a C1s binding energy had significantly changed in AECC fiber. The binding energy of C1s in amidoxime fibers was 286.14 eV, the binding energy of C1s in AECC was 286.09 eV. It demonstrated that the binding energy of carbon in -C=N- was changed. The binding energy of O1s in amidoxime fibers was 532.37 eV, the binding energy of O1s in AECC fibers was 532.00 eV. The reason is that a coordination bond was formed between the -OH groups in amidoxime fibers and the rare earth ions Eu (III), and the oxygen during new chemical environment was produced. Meanwhile, the bonded hydrogen state became the coordination state with the rare earth ion Eu (III), hence the bonds were strengthened. The combined IR analysis and significant changes of the fibers color before and after the reaction mutually demonstrated the coordination of -OH group and the rare earth ions Eu (III). The binding energy of N1s in AECC fibers increased slightly to 399.33 eV compared to the binding energy of N1s in amidoxime fibers (399.26

eV). It demonstrated that the coordination had occurred between N in  $-N_2H-$  and rare earth ions. Meanwhile, the electron energy of rare earth ions Eu (III) were all changed, which proved that the rare earth ions involved in the coordination reaction.



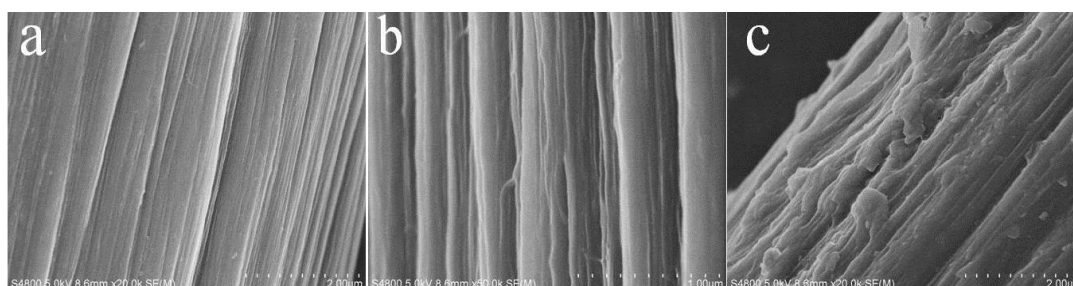
**Figure 1:** XPS spectras of different elements and AECC fibers: a - e are the binding energies of C1s, O1s, N1s, Eu (III) elements and AECC fibers

**Table 3:** The binding energy of different elements and AECC fibers

RARE EARTH IONS	AMIDOXIME FIBERS	AECC FIBERS
C1s	284.14	284.09
O1s	532.37	532.00
N1s	399.26	399.33
Eu (III)	--	1135.7

### 3.4 Morphology of AECC fibers

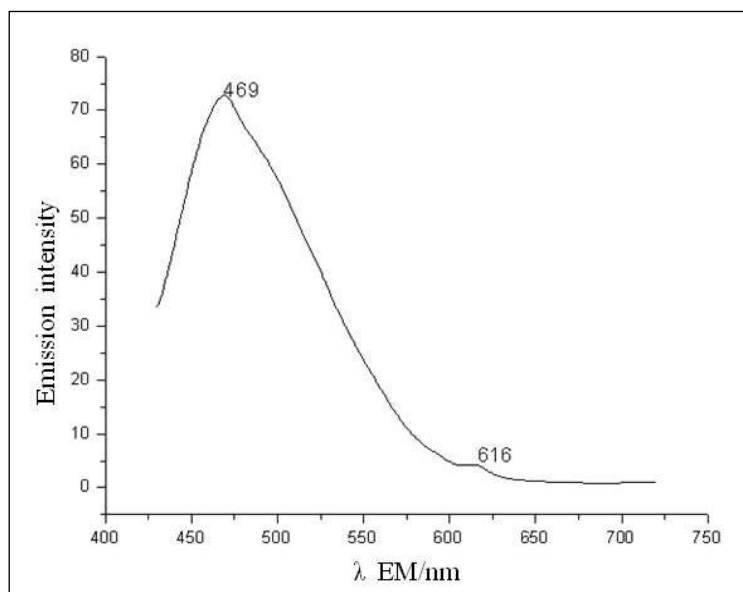
In Figure 2, the scanning electron microscope (SEM) photograph of the PAN fiber surface is uniform and smooth and has no obvious defects. While the surface of amidoxime fiber after reaction with hydroxylamine solution maintained a relatively smooth apparent morphology, some uniform rough dents were observed, which showed the apparent of PAN fiber changed after amidoxime. Hence, the emergences of a number of defects were induced on the surface of the fibers. AECC fibers produced by the reaction of Europium (III) solution had rougher surface and more significant jagged dents, which showed that amidoxime fibers and rare earth solution had a full reaction, and the surface of the fibers was coordinated a large amount of rare earth ions. And they were uniformly distributed onto the surface of the fibers; meanwhile, it also showed the mechanical properties of fiber were affected, so it's breaking strength and elongation at break decreased.



**Figure 2:** SEM images of PAN fibers (a), amidoxime fibers (b) and AECC fibers (c).

### 3.5 Fluorescence spectra of AECC fibers

The electronic arrangement formula of Eu (III) is  $4f^76s^2$ , the f shell electron of its secondary outer layer electron is unfilled, and it belongs to be paramagnetic. In addition, the excited state of the ion ( $m^*$ ) energy layer (i.e. the  $f^*$  energy layer which is transferred from f energy layer) located below the lowest excited state energy layer of the ligand, and there are no multi energy layers between  $m^*$  and  $s_0$  energy layers. Thus, the ions can emit linear characteristic luminescence. The spectrum was determined under the conditions of 10 nm incident and emission slit at room temperature. The characteristic peaks of AECC fibers appeared at the excitation wavelength of 380 nm, and AECC fibers appeared two bands, either of which the 469 nm luminescence bands might be ligand luminescence emission and it was luminescence emission band of Eu (III) at the 616 nm.



**Figure 3:** fluorescence spectra of AOCF-Eu (III) complexes fiber

### 3.6 Mechanical properties of AECC fibers

The breaking strength and elongation at break of fiber samples were measured for 50 times using electronic single fiber strength tester (LLY-068). The breaking strength and elongation at break of PAN fibers were 0.71 cN and 18.29%, their sample variances were 0.0017 and 2.47, respectively. The breaking strength and the elongation at break of amidoxime fibers were 0.68 cN and 19.86%, their sample variances were 0.0026 and 3.31, respectively. The breaking strength of amidoxime fibers was lower than that of the acrylic fiber (PAN). The reason is that after amidoxime reaction of the -CN in PAN, the polymer chain on the appearance of fiber became uneven and part of the polymer chain fractured, so the surface tension of the fiber declined while elongation at break increased. The fibers became thinner, the elastic of fibers became better, and the sample variance of test values before and after the reaction became larger, data became scattered. It illustrated that the unstable properties of the fibers maybe induced by the damage of fiber during the process of reaction.

The relationships among different Eu (III) content and breaking strength and elongation at break of fiber were derived (Table 4). As can be seen from Table 4, the breaking strength and elongation at break of fiber decreased with the increase of content of Eu (III). There are two reasons. First, when amidoxime groups coordinated with Eu (III), a body structure can be formed because one Eu (III) ion can coordinate with two amidoxime groups on different strand of fiber, so the elastic of the fibers decreased. Second, soaking solution with different pH and temperature can cause the swelling and corrosion role on the fiber, and some physical adsorption also destroyed the fiber polymer structure, hence the elasticity of original fibers was decreased. Compared to the PAN fibers, the breaking strength and elongation of AECC fibers were all decreased with the increase of the content of Eu (III) ion. But, the produced AECC fibers possess a good ability for yarn spinning.

**Table 4:** The relations among different content of Eu (III) and tensile property of AECC fibers

CONTENT OF EU (III) /(MG-G-1)	BREAKING STRENGTH /CN	ELONGATION AT BREAK /%
5.65	0.695	18.30
6.67	0.612	17.93
23.55	0.603	17.56
60.95	0.584	16.83
90.69	0.522	16.27

Note: A is Eu (III) (mg) / amidoxime fiber (g)

#### 4. CONCLUSIONS

In this work, the AECC fibers were successfully prepared by chelating reaction using amidoxime fibers (made from PAN fibers) and Europium oxide. The highest Eu (III) content can be harvest when the optimum reaction condition was set at pH = 3.0 and temperature = 45 °C, time = 5 hours. Meanwhile, the fluorescence of the AECC fibers was the highest among other groups according to the results of a series of measurements. The emission intensity of AECC fibers increased as the increasing content of Eu (III). When the amidoxime group fully reacted, the AECC fibers would occurred "concentration quenching" phenomenon with the increasing content of Eu (III). The mechanical properties of AECC fibers declined as the increasing content of Eu (III). In conclusion, this study provided a theoretical basis for the preparation and practical application of fluorescent fibers.

#### 5. ACKNOWLEDGEMENT

The work is supported by Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), National Natural Science Foundation of China under grant Nos. 20771002 & 11372205 and Project for Six Kinds of Top Talents in Jiangsu Province under grant No. ZBZZ-035, Science & Technology Pillar Program of Jiangsu Province under grant No. BE2013072

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