Study on Preparation and Properties of Luminescent Polyamide Fiber Doped with Graphene

Haiyan Ni*, Yonggui Li and Zhi Chen
Fujian Key Laboratory of Novel Functional Textile Fibres and Materials, Minjiang University, Fuzhou, 350108, China.
Email: mjuhaiyan@163.com

Abstract. In order to improve the mechanical properties and spinning performance of luminescent nylon fibers, different proportions of graphene were used for melt spinning, and the best spinning process of graphene-doped luminescent nylon 150D/36F composite fiber was found. The effects of doped graphene on the mechanical properties, molecular structure and luminescent properties of luminescent nylon fibers were analyzed by means of electron microscope scanning, infrared spectroscopy, test instrument of long afterglow properties and monofilament strength tester. The experimental results show that the mechanical properties of the fiber are improved after graphene is doped into the luminescent nylon. Considering the luminescent properties and mechanical properties of the fiber, the comprehensive properties of the fiber are the best when the amount of graphene is 0.5‰.

1. Introduction

Rare earth luminescent materials have excellent luminescent properties, and their luminescent properties play an important role in wearing, household and decoration. Luminescent fiber not only has the same properties as ordinary fiber, but also has the characteristics of light gathering during the day and luminescence at night, so it is deeply concerned by researchers in the textile field. However, it is found that the strength of nylon fiber decreases greatly after the addition of rare earth luminescent materials, which seriously hinders the expansion of its application field, so it is necessary to study how to improve the mechanical properties of nylon fiber.

Graphene has become a research hotspot in functional textiles in recent years because of its special structure, strong fracture strength and improving the mechanical properties of materials. For example, Liu Xia studies the preparation and properties of graphene and its composites, which shows that graphene composites have better mechanical properties. Sun Kaikai, Tian Mingwei and others studied the preparation and properties of graphene modified nylon filament, and the results showed that the sun aging resistance of the fiber was improved. Ma Yong, Wang Shuangcheng, Lu Dongsheng and others have studied the preparation and properties of biomass graphene modified polyamide 6 masterbatch and fiber, which shows that graphene is feasible to improve the fiber properties. I explored the effect of graphene on luminescent nylon fiber, and improved the mechanical properties of luminescent nylon fiber by doping graphene, and improved its market application prospect in decoration, household use and clothing.
2. Experimental

2.1. Materials

Polyamide 6 chips are produced by Changle Liheng Nylon Technology Co., Ltd.; KH876 rare earth aluminate luminescent materials, flow stabilizers, oxidation stabilizers, anti-UV agents, cross-linking agents, dispersants and other auxiliaries are purchased from Dalian Luming Technology Group Co., Ltd.; Graphene nylon masterbatch is prepared by in-situ polymerization by the Chinese Academy of Sciences; Spinning oil is provided by Changle Liheng Nylon Technology Co., Ltd.

2.2. Preparation of Luminescent Nylon Fiber Doped Graphene

High concentration rare earth luminescent masterbatch, graphene masterbatch and PA6 chips were mixed according to different proportions. Taking PA6 as the fiber matrix, the addition ratio is calculated according to the overall ratio of 100, the luminescent content accounts for 8%, and the graphene content accounts for 0‰, 0.1‰, 0.5‰, 0.8‰, 1‰, 1.2‰ respectively. The composition of the fiber is shown in Table 1. After the material is mixed and dried, the reasonable melt spinning process of FCF-3 small spinning machine is adjusted, the spinning process flow chart is shown in figure 1, and the doped graphene luminescent nylon composite fiber is spun.

| Sample numbers | PA mass fraction | Mass fraction of luminescent powder to PA/0 | Mass fraction of graphene to PA /00 |
|----------------|-----------------|------------------------------------------|----------------------------------|
| 1#             | 100             | 8                                        | 0.0                              |
| 2#             | 100             | 8                                        | 0.1                              |
| 3#             | 100             | 8                                        | 0.5                              |
| 4#             | 100             | 8                                        | 0.8                              |
| 5#             | 100             | 8                                        | 1.0                              |
| 6#             | 100             | 8                                        | 1.2                              |

Spinning raw material → Mixing and drying → Stock bin → Screw → Metering
Melt extrusion → Spinneret plate → Exflagellation → Side blow open → Cooling and shaping → Suction
Cut tobacco suction → Oil roller → Oiling → Roll 1, Roll 2, Roll 3 → Drafting → Take up roll → Winding

Figure 1. Spinning process flow chart

2.3. Structural Characterization and Performance Testing

2.3.1. Structural characterization of fiber surface morphology

The fiber samples were prepared separately, and the surface morphology of the samples was scanned by Nicolet IS 50 electron microscope (SEM). Adjust the aperture, focal length and microscope magnification to achieve the best image, and observe its micro-shape.

2.3.2. Characterization of fiber by infrared spectroscopy

The structure of the sample was determined by IR-960 Fourier transform infrared spectrometer. The 1mg sample and pre-dried 200mg potassium bromide were ground evenly and kept at 12.5 MPa for 1 min, and then tested. The scanning range is 4000~500cm⁻¹ and the resolution is 4cm⁻¹.

2.3.3. Test of fiber linear density and mechanical properties

Refer to GB/T 14335 - 2008 "Chemical fiber - Test method for linear density of short fibers", the linear density of fibers was measured by XD-1 fiber fineness meter, the test range is 0.8 to 40.0 dtex, the clamping length is 20 mm, and the measurement error is less than ±2%.
Refer to GB/T 14337–2008 “Chemical fiber - Test method for tensile properties of staple fibers”, the tensile strength and elongation at break of the fiber were measured by XQ-1 monofilament strength tester. The fiber clamping length is 20 mm and the drawing rate is 5 mm/min. Each sample was repeatedly measured 20 times, and the results were averaged.

2.3.4. Fiber boiling water shrinkage test
The boiling water shrinkage of the fiber was determined according to GB/T 6505-2008 "Chemical fiber - Test Method for Thermal Shrinkage of Filament". The fiber was wrapped in gauze and treated with boiling water in a constant temperature water bath for 30 min. After natural drying, it was placed in the standard state for 24 h. The shrinkage of boiling water is calculated according to the following formula.

\[ S = \frac{L_0 - L_1}{L_0} \times 100\% \]  

In the formula: \( S \) is the shrinkage of boiling water, %; \( L_0 \) is the skein length before boiling water treatment, mm; \( L_1 \) is the skein length after boiling water treatment, mm.

2.3.5. Fiber luminescent intensity test
The sample to be tested was placed in the dark for 12 hours to ensure that the afterglow is completely decayed. The afterglow luminance of the sample was measured by PR-305 afterglow luminance tester, the excitation illuminance was 1000lx, the excitation time was 15min, and the afterglow sampling time was 10h. The luminescent properties of the samples were analyzed.

3. Results and Discussion

3.1. Design of Spinning Process Parameters of Doped Graphene Luminescent Nylon
After repeated comparative analysis of many experiments, the best spinning process of 150D/36F doped graphene luminescent nylon is obtained, and the process parameters are shown in Table 2.

3.2. Spinnability of Doped Graphene Luminescent Nylon Filament
FCF-3 spinning machine was used to spin doped graphene luminescent nylon filament by melting spinning method. In the spinning experiment process, the filaments were produced smoothly, the surface was smooth, and there was no frizz. The filament is easily wound to the drawing roller and winding roller, and finally wound on the bobbin. Therefore, graphene doped nylon filament has good spinnability. The effect of filament sample is shown in figure 2.

| Heating area | Temperature / °C | Operating mechanism     | Rotational speed/(r/min) |
|--------------|-------------------|-------------------------|--------------------------|
| Screw zone 1 | 248               | Roll 1                  | 292                      |
| Screw zone 2 | 250               | Roll 2                  | 760                      |
| Screw zone 3 | 252               | Roll 3                  | 965                      |
| Screw zone 4 | 254               | Metering pump           | 9.08                     |
| Screw zone 5 | 256               | Winding roller          | 965                      |
| Handpiece    | 258               |                         |                          |
| Roll 1       | 80                |                         |                          |
| Roll 2       | 110               |                         |                          |
| Roll 3       | 125               |                         |                          |
3.3. The Effect of Doped Graphene on the Micro-morphology of the Fiber Surface

Figure 3 is an SEM image of graphene luminescent nylon fibers doped with different proportions. It can be seen from the figure that all the samples are cylindrical, which is because the spinnerets of this fiber melt spinning are round holes. The surface of the fiber filament is uneven and adhered to a small amount of granular material, which is mainly due to the fact that the luminescent nylon fiber is mixed with rare earth luminescent materials, and the added materials are not evenly dispersed in the spinning process; In order to improve the mechanical properties of luminescent fibers, different proportions of graphene were doped in this experiment. Because the graphene particles are nano-sized and the proportion of graphene added is small, the appearance effect of the above fibers does not change much.

Figure 3. SEM image of luminescent nylon doped with different proportions of graphene. Figure (a) ~Figure(d): The contents of graphene in the luminescent fiber are as follows: 0‰, 0.1‰, 0.5‰ and 1‰.
3.4. Effect of Doped Graphene on Fiber Chemical Structure

Figure 4. Infrared spectrum of doped graphene luminescent nylon fiber.

Figure 4 shows the infrared spectrum of luminescent nylon fibers doped with graphene in different proportions. It can be seen that the samples all have absorption peaks of amino groups at 3293.36 cm\(^{-1}\), and absorption peaks of methylene groups at 3071.12 cm\(^{-1}\) and 2928.45 cm\(^{-1}\). 1638.22 cm\(^{-1}\) is the absorption peak of amide I caused by C=O, and 1539.46 cm\(^{-1}\) is the absorption peak of amide II caused by N-H and C-N deformation vibration. Therefore, the sample contains a polyamide component. Moreover, there are characteristic peaks representing graphene in the sample 2#~6#, such as the absorption peak caused by the bending vibration of C-OH at 1633.48 cm\(^{-1}\) and the absorption peak of C-O-C at 1119.22 cm\(^{-1}\), but the infrared spectral orientations of all samples are roughly the same, so the doping of graphene does not affect the molecular structure of nylon.

3.5. Effect of Doped Graphene on Mechanical Properties of Fiber

Table 3. Composition of luminescent nylon fiber.

| Sample No | Breaking strength(cN/dtex) | Elongation at break(%) | Boiling water shrinkage |
|-----------|----------------------------|------------------------|------------------------|
| 1#        | 1.78                       | 8.74                   | 11.87                  |
| 2#        | 2.17                       | 9.73                   | 10.31                  |
| 3#        | 2.31                       | 10.16                  | 9.98                   |
| 4#        | 2.35                       | 10.33                  | 9.73                   |
| 5#        | 2.39                       | 10.51                  | 9.57                   |
| 6#        | 2.41                       | 10.75                  | 9.41                   |

It can be seen from Table 3 that the breaking strength, elongation at break and boiling water shrinkage of luminescent nylon fiber are improved with the increase of graphene doping amount. With the increase of the amount of graphene, the breaking strength of the fiber increased by 35.3%, the elongation at break improved by 22.9% and the boiling water shrinkage of the fiber changed by 20.7%. This is because graphene, a new functional material, has the advantages of high strength and high elastic modulus, and it plays an important role in improving the mechanical properties of nylon filament.
3.6. Effect of Doped Graphene on Luminescent Properties of Fiber

The long afterglow fluorescence test of graphene luminescent nylon fiber with different proportion is carried out, and the test results are shown in figure 5. It can be seen from the picture that both luminescent nylon and graphene-doped luminescent nylon have experienced a fast decay stage and a slow decay stage. With the increase of graphene content, the fluorescence initial brightness of luminescent fiber will decrease, and with the increase of graphene content, the brightness decline rate of luminescent fiber will increase, and the luminescent time will become shorter. In the picture, the afterglow brightness of the luminescent nylon fiber is the largest and the effective afterglow time is the longest. When the graphene content is less than 0.5 ‰, the fiber luminance is slightly lower than that of the luminescent nylon fiber, and when the graphene content is more than 0.5 ‰, the fiber brightness decreases obviously.

4. Conclusion
The best process parameters for preparing graphene luminescent nylon: zone 1 is 248 °C, zone 2 is 250 °C, zone 3 is 252 °C, zone 4 is 254 °C, zone 5 is 256 °C, handpiece is 258 °C. The speed of metering pump is 9.08 r/min, the speed of one roller is 292 r/min, the speed of two rollers is 760 r/min, the speed of three rollers is 965 r/min, and the winding speed is 965 r/min.

The test results of fiber mechanical properties show that doped graphene can improve the breaking strength and elongation at break of luminescent nylon, and the boiling water shrinkage test results show that the dimensional stability of doped graphene luminescent nylon has been improved.

The results of fluorescence afterglow test showed that the afterglow property of graphene-doped luminescent nylon decreased. When the graphene content was less than 0.5 ‰, the luminance of the graphene-doped fiber was slightly lower than that of the luminescent nylon fiber, and when the graphene content was more than 0.5%, the luminance of the fiber decreased obviously. Therefore, considering the luminescent performance and mechanical properties of the fiber comprehensively, the comprehensive performance of the luminescent nylon fiber is the best when the graphene content is 0.5‰.

5. Acknowledgments
We appreciate for the financial support from the “Project of Central Leading Local Science and Technology Development (No. 2018L3012)”, “The Open Project Program of Fujian Key Laboratory of Novel Functional Textile Fibers and Materials (Minjiang University), China (No.FKLTFM1724)” and “Science and technology projects of Fujian Province (No. 2019H6019)”.

6. Reference
[1] Wang Rong. Preparation of fluorescent fiber and its properties [D]. Donghua University, 2015.
[2] Xu Yingtong. The application of luminescent fiber in children's home lighting [D]. Beijing Institute of Clothing Technology, 2016.
[3] Dong Chenxue, Liu Yongmei. The development of luminescent fiber and its application analysis in textile and clothing [J]. Biotechnology World, 2013, 10(07): 168.
[4] Zhao Jumei, Gao Xiaoliang. Application of rare earth long afterglow luminescent materials in textiles [J]. Textile Industry and Technology, 2010, 39(06): 38-40.
[5] Wang Lanting. The properties of luminescent fiber and its application in warp knitting [D]. Jiangnan University, 2007.
[6] Lv Wenjun. Preparation and research of rare earth fluorescent nylon 6 [D]. Donghua University, 2008.
[7] Yang Liyue, Jin Xiaojing, Yang Qingbin, et al. Research on the basic properties of luminescent fiber [J]. Shandong Textile Science and Technology, 2017, 58(03): 11-13.
[8] Yang Wenbin, Zhang Li, Liu Jingwei, et al. Progress in the preparation and application of graphene composite materials [J]. Materials Engineering, 2015, 43(03): 91-97.
[9] Li Jiming, Wu Suisheng, Yang Mei. Application research of functional graphene textiles [J]. Chemical Fiber and Textile Technology, 2017, 46(01): 11-15.
[10] Wang Yujiao, Tian Mingwei, Qu Lijun, etc. Research status and development trend of graphene[J]. Journal of Chengdu Textile College, 2016, 33(01): 1-18.
[11] Liu Xia. Study on preparation and properties of graphene and its composite materials [D]. Donghua University, 2016.
[12] Sun Kaikai. Preparation of graphene modified polyamide filament and its resistance to sunlight aging[D]. Qingdao University, 2015.
[13] Sun Kaikai, Tian Mingwei, Qu Wenguang, et al. Preparation and properties of graphene modified nylon filament[J]. Cotton Textile Technology, 2015, 43(11): 24-28.
[14] Ma Yong, Wang Shuangcheng, Lv Dongsheng, et al. Preparation and properties of biomass graphene modified polyamide 6 masterbatch and fiber [J]. HeFiber, 2017, 46(10): 6-10.
[15] Liu Peng. Preparation and properties of flame-retardant polyamide 6 and fibers [D]. Donghua University, 2015.