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Improvement of color value of bio-based polyamide 56 fibers

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Abstract: This paper introduces a feasible method to improve the color value of bio-based polyamide 56 (PA56) fiber. Three types of whitening modifiers were introduced into the bio-based PA56 fibers by the *in-situ* polymerization method and melt blending method in order to improve the fiber color. The color values and mechanical properties of PA56 fibers were tested and analyzed and the optimum additive ratio and process conditions were discussed. The results show that the improved color value of bio-based PA56 fibers can be achieved by the melt blending method of fluorescent whitening masterbatch and reasonable spinning condition control. When the additive amount of fluorescent whitening agent is 0.3%, the index of lightness (L) increased from 84 to 90, while the yellow index (YI) reduced from 16.8 to 12.6. Moreover, PA56 fibers show high breaking strength about 4.27 cN/dtex and good yellowing resistance and durability.

Keywords: bio-based fiber; color values; fluorescent whitening; polyamide 56.

1 Introduction

The shortage of petroleum resources and the serious over-capacity of in the chemical fiber industry have been global issues for many years (1–3). There is an urgent need to upgrade and transform this problem. In recent years, China has witnessed more research breakthroughs, scientific advancement and product innovation. The development of bio-based fibers is one of the major breakthroughs. However, under certain circumstances bio-based fibers easily turn yellow, which remains to be the major problem in the production of bio-based fibers.

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Bio-based polyamide 56 (PA56) shares many similarities with the polyamide 6 and polyamide 66, such as good moisture absorption (4–7), dyeing and antistatic properties, softness and low costs. Thus, it has great opportunities for development. However, polyamide is susceptible to become yellow when exposed to the light or sunshine (3, 8, 9). As for bio-based PA56, the raw materials, including bio-based adipic acid and pentanediamine, are generated from glucose, which is fermented by microorganisms. Thus the residual lignin inside is easily oxidized in the air and turned into the so-called chromophore (1, 2). The chromophore further deepens the yellow color of the fibers. The problem limits the application and development of bio-based PA56.

In this paper, three types of whitening modifiers such as a fluorescent whitening agent and cobalt acetate were introduced into the bio-based PA56 fibers by the *in-situ* polymerization method and the masterbatch melt blending method as added in order to improve the fiber color. The color values including the index of lightness (L), gray scale value (B) and yellowness index (YI) of PA56 fibers were tested and analyzed, and the optimum additive ratio and product technology are discussed. The results show that the improved color value of bio-based PA56 fiber can be achieved by the melt blending method of the fluorescent whitening masterbatch and reasonable spinning technology control.

2 Experimental

2.1 Materials

Bio-based adipic acid and bio-based pentamethylene diamine were purchased from DuPont (Wilmington, DE, USA). Fluorescent whitening agent OB-1 was purchased from Shanghai Maigao Chemical Co., Ltd. (Shanghai, China). Purple degrees agent (RSD) and blue degrees agent (RIs) were purchased from Shanghai Hengcai Chemical Industry Co., Ltd. (Shanghai, China). Cobalt acetate was purchased from Nanjing Anyang Chemical Industry Co., Ltd. (Nanjing, China). PA56 and PTT (polytrimethylene-terephthalate) was purchased from DuPont.

2.2 Synthesis and spinning of PA56

PA56 was prepared via the *in-situ* condensation polymerization reaction by firstly using bio-based adipic acid and bio-based pentamethylene diamine as monomers, then adding RSD and R1s, fluorescent whitening agent OB-1 and cobalt acetate as modifiers. The additive amounts of modifiers were 0.1%, 0.15%, 0.20%, 0.25% and 0.30% to the polymer mass. The polymerization temperature was between 290°C and 300°C, polymerization time was 5–6 h, the vacuum degree was -0.10 to -0.03 MPa.

The modified masterbatch was prepared by melt blending with a twin screw based on the mass ratio of 10% modifier, 10% PTT and 80% PA56. All materials were dried before blending. PA56 chips were dried at 165°C for 8 h with nitrogen protection. The prepared masterbatch was also dried in a vacuum oven at 100–110°C for 5–6 h. Then the spinning experiment was carried out in a TMT spinning and drawing machine. The temperatures of the screw are 282°C, 286°C, 288°C, 291°C, 293°C and 296°C, respectively; the screw's speed was 40–50 rpm, the extrusion process takes 5–8 min, the side cooling blowing was adopted with the air temperature 22–26°C, wind humidity 90–96% and wind speed 0.45 m/s. The spinning speed was 4500 m/min, total drawing ratio was 3 and the hot roller temperature was 160°C.

2.3 Characterization

Intrinsic viscosity: The intrinsic viscosity of PA56 was measured by using an ubbelohde viscometer according to GB/T1632-93 (determination of viscosity number and intrinsic viscosity of polymer dilute solution). A mixing solvent of phenol and cellon (3/2, v/v) was used, and the test temperature was 25°C. The test was repeated at least three times and an average test result was obtained. Standard deviation is controlled at ± 0.1 dl/g.

Strength test: The strength of PA56 fiber was tested according to GB/T14344 (test methods for tensile properties of chemical filament yarns). The test was repeated for five specimens and the test result obtained was based on the average. Standard deviation is controlled at ± 0.5 cN/dtex.

Linear density test: The linear density of PA56 fiber was tested according to GB/T14343 (test method for linear density of chemical filament yarns). The test was repeated for five specimens and the result obtained was based on the average. Standard deviation is controlled at ± 0.5 dtex.

Chromaticity test: The chromaticity of PA56 fiber was tested according to GB/T 17644-2008 (test method for whiteness and chromaticity of textile fibers) by using 6801 colorimeter (BYK Chemie GMBH, Wesel, Germany). The test was repeated on the three specimens and the result obtained was based on the average. The standard deviation was controlled at ± 0.5 .

3 Results and discussion

3.1 Raw material analysis

Polyamide is susceptible to becoming yellow when exposed to the light or sunshine. As for bio-based PA56, the raw materials including adipic acid and pentanediamine are made by biological fermentation products. Thus the residual lignin impurities are easily oxidized in the air and it produces a chromophore which further deepens the yellow color (3, 8, 10). In addition, as the melting point of bio-based PA56 is about 258°C, the drying temperature and spinning temperature for PA56 are really high. Therefore, the crystallization and drying process as well as the spinning process make this situation worse.

Table 1 shows color values for the biological basis PA56 chip before and after drying. It suggests that before the drying processes, L and YI of PA56 chips are 63.0 and 46.3. After drying at 165°C for 8 h, the YI value increases to 70.3, indicating that the chips turn yellow in this drying process. Meanwhile, the L value reduces and B value increases.

3.2 Modification in the polymerization process

During the polymerization process of bio-based PA56, we added the appropriate amounts of the different modifiers separately, including fluorescent whitening agent OB-1, blue degree agent R1s, purple degree agent RSD and cobalt acetate. Figure 1 shows the effects of different modifiers on L, B and YI of PA56 fibers. The analysis indicates that purple and blue light waves cannot suppress yellow and gray light waves. Therefore, the addition of purple degree agent and blue degree agent has no effect on the color

Table 1: Color values of PA56 chip before and after drying process.

Sample	L	B	YI	W
Before drying	63.0	17.6	46.3	53.2
After drying	52.0	22.3	70.3	78.6

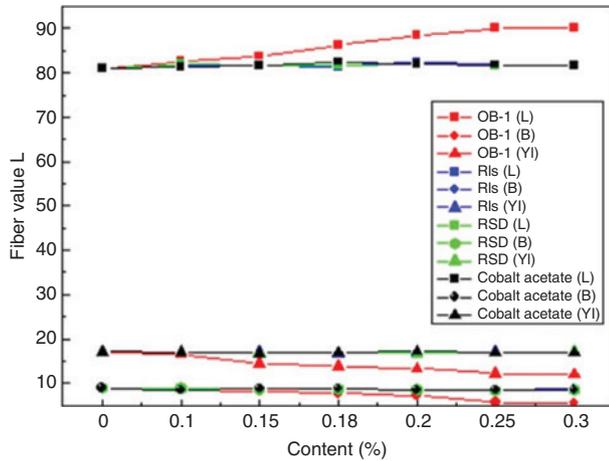


Figure 1: Effects of different modifiers on the color values of PA56 fibers.

values of the bio-based PA56 fibers. Moreover, it can be seen that the addition of cobalt acetate also has no effect on the chromaticity of PA56 fiber.

In addition, the fluorescent whitening agent OB-1 shows a positive effect on the improvement of the color values for PA56 fiber. With the addition of OB-1, the L value gradually increases. Meanwhile, both B and YI values decrease. In this work, the optimum additive amount of OB-1 is 0.2–0.25%. The fluorescent whitening agent in the fiber matrix emits blue fluorescence by absorbing ultraviolet light, which is complementary to yellow light and plays the role of fluorescent whitening.

The effect of the additive amount of OB-1 on the intrinsic viscosity of PA56 is shown in Figure 2. As the additive amount of OB-1 increases, the intrinsic viscosity of PA56 decreases, implying that the addition of OB-1 hinders the

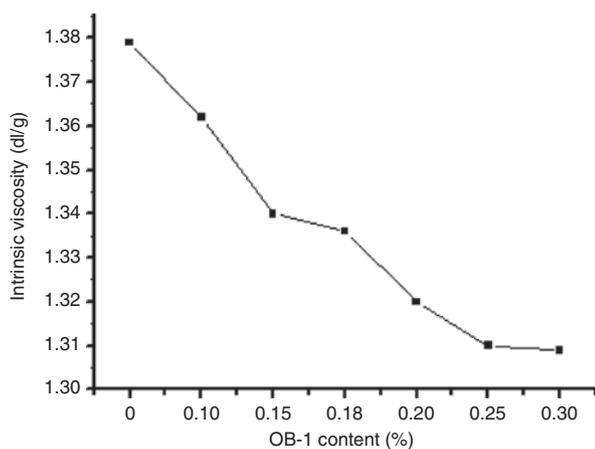


Figure 2: Effect of the additive amount of OB-1 on the intrinsic viscosity of PA56.

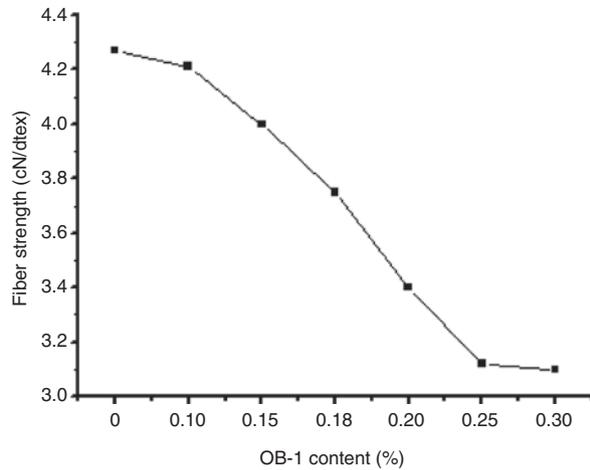


Figure 3: Effect of the additive amount of OB-1 on the fiber strength.

polymerization reaction to some extent. When the additive amount of OB-1 is 0.2%, the intrinsic viscosity of PA56 reduces to 1.32 dl/g. The decrease of molecular weight has a negative effect on the mechanical properties of fibers. As shown in Figure 3, the breaking strength of PA56 fiber reduced with the increase of the additive amount. However, the fiber strength in this work is consistently higher than 3.0 cN/dtex, it can meet the requirement of the finished fabric.

The above results show that addition of blue degree agent, purple degree agent or cobalt acetate during the polymerization process provides no strongly manifested improvement of the whiteness and color values of PA56 fibers. However, for the fiber containing fluorescent whitening agent OB-1, L value increased to 86, the B value dropped to 6.3 and the YI value decreased to 12.9. The improvement of fiber color is obvious. However, fluorescent whitening agent has a negative influence on the polymerization reaction. The conditions of polymerization reaction such as temperature and reaction time should be further adjusted for obtaining the appropriate molecular weight.

3.3 Melt blending modification in the spinning process

For melt spinning of PA56, we adopted two methods to add the masterbatch. They are: (1) injecting masterbatches through a chip down the pipeline in front of the screw, then melting the mixing masterbatches and PA56 evenly in the screw spinning after the screw; (2) injecting masterbatches into the melt on-line by the addition of a device in by-pass form on the backside of the melting pipeline, leading the molten liquid to flow out the main pipeline and then mixing it with modified master-batches; this is then spun

after blending twice using a dynamic mixer and a static mixer. In this paper, we analyzed the fluorescent whitening modification in the spinning process for a bio-based polyamide FDY fiber (77 dtex/48 f) as an example.

3.3.1 Drying conditions

As illustrated in Section 3.1, after drying at 165°C for 8 h, the chips turn yellow. The YI increased from 46.3 to 70.3. In addition, the amide is easily oxidized by heat and breaking, which decreases the molecular weight and fiber strength (1, 11). However, PA56 has a lot of unsaturated hydrogen bonds and hydrophilic groups in the molecular chain; in order to ensure the spin ability, it is very necessary to remove the moisture from the chips. Therefore, we adopted a relative low drying temperature of about 155°C and a long drying time for 10–12 h with nitrogen protection. After the drying process, the moisture content of the dried chip is about 23 ppm. Similarly, the modifiers before melt blending and the masterbatches before spinning need to be dried at 100–110°C for 5–6 h in vacuum.

The method of injecting masterbatches through chips down a pipeline in front of the screw requires the dry conditions to be higher than in the method of injecting masterbatches through the melting on-line addition device in a by-pass form on the backside of the melting pipeline. If the drying effect is not good, it is easy to produce link of plugging material in the feed end of the screw, production difficulties, fluorescent whitening modifying the masterbatch feeding fluctuation, fluorescent whitening agent distribution uneven and the modification effect is poorer.

3.3.2 Spinning process

The melting point of PA56 is about 258°C, the spinning temperature should be 20–40°C higher than its melting point. Considering that the bio-based PA56 is susceptible to yellowing and heat oxidation, nitrogen protection and a middle high spinning temperature must be used. However, if the spinning temperature is too low, the chips are difficult to melt completely and the screw is easily damaged because of much higher shear forces. In this work, the temperatures of different zones in the screw are 282°C, 286°C, 288°C, 291°C, 293°C and 296°C, respectively. In order to avoid the chip melting early in front of the screw and prevent the melted materials from flowing back, the temperature in the first zone must be the lowest one. In addition, the screw production area is protected by nitrogen. The suitable spinning temperature ensures that the loss of the intrinsic viscosity after the spinning process is less than 0.003 dl/g.

The cooling conditions in the spinning process is very important. In order to ensure the softness of the fiber and reduce the internal stress of filaments, the cooling condition should be mild with a higher wind temperature and humidity, and lower wind speed. This is helpful for the improvement of the spinning forming and fiber properties. However, if the cooling conditions are too mild, the melt cooling cannot finish completely in the spinning process, which influences the drawing and deformation process of the fibers, as a result causing fiber defects and damaging the fiber strength (3, 12). Experiments show that the following conditions are appropriate: side wind temperature 22–26°C, wind speed 0.35–0.45 m/s and wind humidity 90–96%. The PA56/masterbatch blends showed good spinnability, no broken filaments appeared in the spinning process.

The drawing condition are also important for the necessary fiber tensile property. If the draw ratio is too high, the fiber monofilament fractures easily, forming fuzziness or aegagropilus. And the stress in fibers would be too great to make fiber tubes deform seriously, thus affecting the unwinding performance. We used the two-step-drawing method to produce FDY fibers. The experiments show that the pre-stretch draw ratio of 1.05–1.10 and draw ratio of 2.2–2.6 are relatively appropriate. When the draw ratio increased to 3.0, the fuzziness or aegagropilus on the fiber surface became more obvious. The first and second hot roller drawing temperatures were set at 82–96°C and 108–128°C, respectively. If the first hot roller heating was closed, the elastic of fiber increased, and the boiling shrinkage rate rose greatly. The fabric or cloth fabricated by these fibers would shrink after the dyeing and finishing process.

PA56 has good hygroscopicity, therefore, in general, it does not easily generate static charge. To avoid oil pollution in the weaving process, the oil ratio can be slightly lower. However, if the oil content is too low, it tends to increase the frictional force between fibers and equipment parts, causing unwinding tension fluctuations (13). In this work, F-2582 nylon FDY spinning oil (Matsumoto Company, Chiba, Japan) was used and the oil rate was set in the range of 1.50–2.0%.

3.3.3 Physical properties of PA56 fibers

The physical properties of bio-based PA56 FDY fibers (77 dtex/48 f) with different additive amounts of OB-1 are shown in Table 2.

It can be seen that the addition of a fluorescent whitening agent into PA56 fibers by the melt blending method can effectively improve the chromaticity of fiber products. The L value increases, while the B and YI values decrease.

Table 2: Effects of the additive amount of OB-1 on physical properties of PA56 fibers.

OB-1 content (%)	Breaking strength (cN/dtex)	Color value		
		L value	B value	YI value
0.00	4.27	81.0	9.0	17.2
0.10	4.27	82.6	8.6	16.6
0.15	4.26	83.8	8.2	14.5
0.18	4.24	86.2	7.8	13.9
0.20	4.25	88.5	7.3	13.4
0.25	4.26	90.1	5.7	12.2
0.30	4.27	90.1	5.6	12.1

Table 3: The change of color values for bio-based PA56 fiber with time.

Color value	1 week	1 month	3 months	6 months	12 months
Value L	90.1	90.0	90.2	90.1	90.0
Value B	5.5	5.7	5.6	5.7	5.8
Value YI	12.0	12.1	12.0	12.2	12.2

When the OB-1 additive amount is 0.3%, the B and YI values drop to 5.6 and 12.1, respectively. More importantly, the addition of OB did not decrease the fiber strength. The tensile strength of 77 dtex/48 f PA56 FDY fiber is about 4.27 cN/dtex. Compared with the *in-situ* polymerization method, the melt blending method is more suitable for preparing whitening bio-based PA56 fiber.

3.3.4 Yellowing resistance

In order to research and analyze the persistence of the fluorescent whitening fiber modifying effect, the melt blending fluorescent whitening fiber is packed and stored as a standard product in 27°C and a humidity of 85%. The color values were tested after different periods of time. The result is shown in Table 3. The color value of the modified fiber showed no obvious change within 1 year, implying good yellowing resistance and durability. The fiber can satisfy the requirement of product usage and storage.

4 Conclusions

In this work, three types of whitening modifiers such as fluorescent whitening agent and cobalt acetate were introduced into the bio-based PA56 fibers by the *in-situ* polymerization method and the melt blending method in order to improve the fiber color. The color values and mechanical

properties of PA56 fibers were tested and analyzed and the optimum additive ratio and process conditions were discussed. The addition of fluorescent whitening agent by the *in-situ* polymerization method can improve the color value of PA56 fibers, but can also reduce the strength of the fiber. The melt blending method of the fluorescent whitening masterbatch is a better way to improve the color value of PA56 fiber. The conditions in the drying, spinning and drawing processes should be carefully adjusted and controlled. When the additive amount fluorescent whitening agent is 0.3%, L increased from 84 to 90, while YI reduced from 16.8 to 12.6. Moreover, PA56 fibers show high breaking strength about 4.27 cN/dtex and good yellowing resistance and durability.

References

- Zhang S, Ma J. The research on the production of bio-based polyamides 56 sheath-core composite modified fiber. *Int J Mater Sci Appl*. 2016;5(2):79–83.
- Zhang S, Ma J. The research on fluorescent modification of bio-based polyamides 56. *Matec Web of Conferences*. 2017;110(1):7–12.
- Cui X, Yan D. Preparation characterization and crystalline transitions of odd-even polyamides 11,12 and 11,10. *Eur Polym J*. 2005;41(4):863–70.
- Jiang JD, Zhang K, Liu CY, Wu GZ. Aliphatic polyamide thermal expansion behavior research. *J Polym Mater*. 2013;13(2):255–62.
- Yu WC. The analysis on physical properties and spinnability of nylon 56. *Polyester Industry*. 2014;26(1):38–9.
- Yu H, Yang M. Discussion on PET/PTT compound fiber technology. *Synth Fiber*. 2011;26(6):53–5.
- Villaseñor P, Franco L, Subirana JA, Puiggali J. On the crystal structure of odd-even nylons: polymorphism of nylon 5,10. *J Polym Sci Part B: Polym Phys*. 1999;39(17):2383–95.
- Franco L, Subirana JA, Puiggali J. Structure and morphology of odd polyoxamides [Nylon 9,2]. A new example of hydrogen-bonding interactions in two different directions. *Macromolecules*. 1998;31(12):3912–24.
- Magill JH. Spherulitic crystallization Part I. “Odd-Even” polyamides: nylon 56 and nylon 96. *J Polym Sci A*. 1965;3(3):1195–219.
- Guibo Y, Qing Z, Yahong Z, Yin Y, Yumin Y. The electrospun polyamide 6 nanofibre membranes used as high efficiency filter materials: filtration potential, thermal treatment, and their continuous production. *J Polym Sci*. 2013;36(2):1061–9.
- Samanta S, He J, Selvakumar S, Lattimer J, Ulven C, Sibi M, Bahrnd J, Chisholm BJ. Polyamides based on the renewable monomer, 1,13-tridecane diamine II: synthesis and characterization of nylon 13,6. *Polymer*. 2013;54(3):1141–9.
- Morales-Gómez L, Soto D, Francoand L, Puiggali J. Brill transition and melt crystallization of nylon 56: an odd-even polyamide with two hydrogen-bonding directions. *Polymer*. 2010;51(24):5788–98.
- Zong Y. Preparation and properties of nano composite metal oxides/polyamide composite fiber. *Synth Fiber*. 2013;42(3):1–6.