

Study on the Structure and Properties of Novel Bio-based Polyamide56 Fiber Compared with Normal Polyamide Fibers

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Abstract. The new kind of bio-based polyamide56 fiber has been synthesized by adipic acid and 1,5-pentanediamine, which was prepared by fermenting a variety of starch. The spin ability, physical and thermal properties of bio-based PA56, PA 6 and PA 66 were evaluated through systematic investigation and measurement. Bio-based polyamide56 resin has been proved to have good spin ability. PA56 have more concentrated distribution of molecular weight than other nylons, which indicated more stable viscosity beneficial for spinning and higher fiber strength. The infrared spectrum showed characteristic amide and methylene absorption peaks of PA56 but different vibration intensities with conventional nylon, which demonstrates different molecular structure. Differential scanning calorimetry combined with thermal gravimetric revealed good heat resistance (the thermal decomposition temperature is 403.7 °C) and high melting-point (254.1 °C) of polyamide56. X-ray diffraction of these fibers were proposed and showed that slightly higher crystallinity of polyamide56 so as to have more regular arrangement of molecular.

Introduction

Polyamide, referred to PA and commonly called nylon, is one of the most important modern industrial materials, which has widespread in many areas of military equipment, automotive and textiles. The most industrial and widely used polyamidefibers currently are polyamide6 and polyamide66, whose raw materials more dependent on petrochemical products. Studies suggest that polyamide56 synthesized by pentamethylene diamine have more perfect performance. But, it is much expensive to produce odd polyamidemonomers by petrochemical methods. Discovering or producing renewable resources to replace petroleum based raw materials is a major concern in terms of both economic and environmental viewpoints [1-3].

There have been decades to displace petrochemical based diamine by fermentation and enzyme methods in lots of big international enterprise such as BASF, Degussa in Europe and Toray, Ajinomoto in Japan, trying to obtain industrialized technology through decarboxylation of lysine which failed to access to markets for the too high cost. More recently, biological pentamethylene diamine technology has made a major breakthrough [4][5]. Pentamethylene diamine were prepared successfully by fermentation from starch in our study. Enzymatic efficiency of microbial strains genetically engineered has been improved greatly, which reduced production costs, so it made quality and price of biological diamine could meet the quality requirements of polyamidepolymerization [6-8]. Joined with Liaoning chemical industry group and other relevant units, logistics department quartermaster equipment institute have been made a large number of studies on polymerization, modification, spinning and other aspects of nylon56, and produced polyamide56 staple fiber and filament yarn successfully for the first time and made the appropriate clothing, which initially solved polymerization and spinning process problems of polyamide56 fiber. At the same time we made a breakthrough in the blended yarn and textile processing of

polyamidefiber, and laid the foundation for the production and development of bio-based polyamidefiber. Bio-based polyamide56 fiber is expected to be advanced materials used in clothing and industrial textiles [9-12]. This paper discusses on several basic performances closely related to applications of textile and apparel.

Material and Methods

Polyamide56 resin, synthesized by pentamethylene diamine and adipic acid, both of which were prepared by fermenting a variety of starch and cellulose in straw, was provided by the quartermaster research institute of the general logistics department. 166dtex/72f PA56 filament was provided by the quartermaster research institute of the general logistics department; 154dtex/36f PA6 filament and 233dtex/ PA6 filament were produced by Guangdong Xinhui meida polyamideCo., Ltd.; 110dtex/34f PA66 filament was provided by Liaoning Yinzhu textile Group Co., Ltd. All the materials are used as obtained.

PA56 resin were spined by single screw spinning machine with a screw diameter of 30mm, spinneret aperture of 0.3mm and 72f. One-trip technology of spinning and drawing was used when spinning with a spinning speed of 2000m/min.

Molecular weight of polyamide fibers were investigated using GPC-2000 gel permeation chromatography (gel column was Waters Styragel @ HT DMF 7.8 × 300mm Column). Took PA6, PA66 and PA56 respectively about 5mg and dissolved in m-cresol of 7-8mL until completely dissolved. The filtrate for use was poured into the sample tube after filtration by syringe.

The total reflection spectra scanning of polyamidefibers were performed on FTIR-BRUKER Tensor27 respectively at 20 C with scanning range of 400 ~ 4000cm⁻¹.

To determine the thermal characteristics, DSC were performed on EXSTAR DSC 6200 differential scanning calorimeter (manufacturer SII) under nitrogen flow at 20mL/min. The samples were heated from room temperature up to 300 C at 20 C/min. Then, samples were (placed in the crucible on the ice) were quickly cooled to 0 C to eliminate the thermal history. Then, samples were cooled to -50 C at 20 C/min and heated again to 300 C at 20 C/min. The glass transition T_g and the melting temperature T_m were determined respectively from the inflection point and the maximum of melting temperature peak. These values were determined on the second heating scan.

TG-DTA combined analyzer of 6300-type was also used to determine the thermal characteristic. The samples (a certain amount in the ceramic crucible) were designed to heat from 30 C to 550 C at 10 C/min. The characteristic degradation temperatures are the temperatures at maximum of the derivative thermo gram curve.

The XRD patterns were obtained with experimental set-up of 1 mm length. In all cases, a linear monochromatic Cu-K_{α1} beam ($\lambda=1.5406 \text{ \AA}$) was obtained using a sealed-tube generator (200W) equipped with a bent monochromator. A Debye-Scherer like geometry was used. The crude film was filled in Lindeman capillaries of 1 mm diameter and 10 mm thickness. The diffraction pattern was recorded on an image plate. Periodicities up to 80 \AA can be measured, and the sample temperature controlled within 0.1Cfrom 20 to 200C.

Results and Discussions

The viscosity of PA56 resin is 145.85, and terminal amino group is 0.0221. The continuous smooth spinning with no bristles under the experimental spinning conditions for 72 hours suggested that PA56 is spinable and spinning smoothly under the experimental spinning conditions .Performance test results of PA56 filament fibers are as shown in Table 1.It is worth mentioning that elongation at break and boiling water shrinkage is too large and strength needs to be improved[13].Therefore, as a new polymer material, related polymer synthesis, preparation and other basic research and technology of PA56 are still in infancy and starve for further study.

Table 1 Performance of PA56fiber

denier, dtex	fracture strength, cN/dtex	elongation at break, %	boiling water shrinkage, %
166	3.9	42	17

Molecular weight and its distribution have a greater impact on the processing performance, mechanical properties, crystallization properties and heat resistance of fiber. Thus, it is very important to determine the molecular weight and its distribution. The molecular weight of the samples measured are as shown in Table 2. Mp is the peak molecular weight. It is obvious that the distribution of molecular weight of polyamide56 is relatively narrow than polyamide6 and polyamide66, which indicates high degree of crystallinity and more stable viscosity beneficial for spinning and higher fiber strength[14][15].

Table 2 The molecular weight of different polyamidefiber samples measured

sample	M _n	M _w	M _p	M _z	M _{z+}	distribution of
PA6	733	112	102	161	210	1.531845
PA66	654	103	889	152	205	1.575487
PA56	636	932	794	131	172	1.465005

IR curves of the measured three polyamidefibers are as shown in Figure 1. Comparative analysis of the position and the peak intensity of each peak shape finds that the peak shape and position of PA56, PA66, and PA6 are different. Table 3 shows part of the attributable spectrum, such as the peak position and vibration intensity of N-H Fermi resonance and stretching resonance in amide II are all different [16][17]. These differences can prove PA56 a new material having different structure from PA6 and PA66.

Table 3 parts of band assignment of different polyamidefibers

PA66	PA6	PA56	band assignment			
peak position (cm ⁻¹)	peak intensity	peak position (cm ⁻¹)	peak intensity	peak position (cm ⁻¹)	peak intensity	
3290	70.7	3290	85.6	3310	82.1	N-H
3070	90.6	3050	95.2	3080	94.3	N-H Fermi resonance and
2930	75.6	2930	89.0	2940	86.7	-CH ₂ -

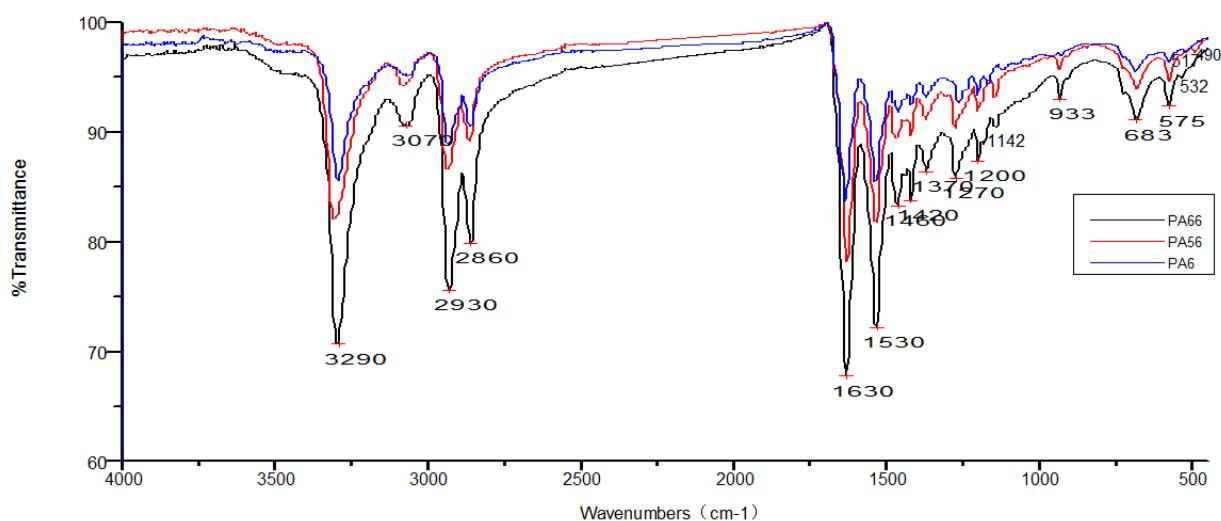


Fig. 1. IR spectra of different polyamidefibers

The thermal behavior of the three polyamidefibers was investigated by DSC. Figure 2 shows the thermal properties of the different fibers. Glass transition temperature(T_g), heats of crystallization(ΔH_c),crystallization temperature(T_c), melting temperatures(T_m), and melting heats(ΔH_m) can be determined and calculated from the DSC thermo grams[18]. The melting temperature of PA6 filaments, PA66 filaments, PA56 filaments obtained from Fig. 2 are 224.2C, 249.3C, 254.1C. The thermal decomposition temperature of PA6 filaments, PA66 filaments, PA56 filaments are 419.8C, 405.0C, 403.7C as shown in Figure 3. There may be slightly differences in results due to different testing methods [19]. Amides groups of PA56 are staggered along the direction of polymer long chain, repeatedly arranged as "5-4-5-4" in the spatial position. So each functional group is capable to form hydrogen bonds [20] in the absence of deformation of the molecule that explain a higher melting point and thermal decomposition temperature. It is mentioning that bio-based polyamide56 have better heat resistance [21] and base of applications at higher temperature than polyamide6.

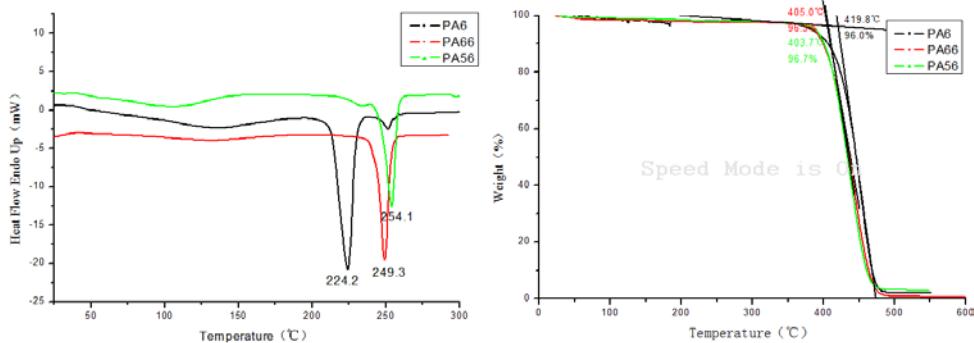


Fig. 2. DSC curves of different polyamidefibers

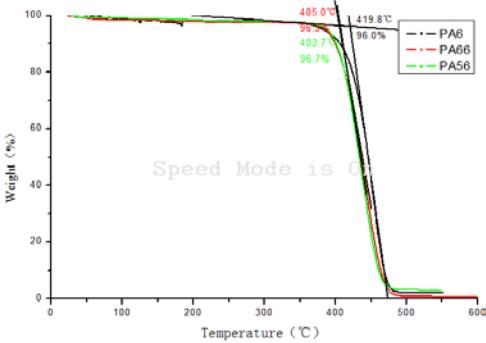


Fig. 3. TG curves of different polyamidefibers

Limited results reported show that the polyamide56 has two polymorphs, fake hexagonal and monoclinic phase at elevated temperatures occur during the Brill transition [22]. Several XRDpolyamidefiber shown in Figure 4 were tested. Apparently from the figure, PA56 has different polymorphs from PA6 and PA66.The result of profile fitting suggests the degree of crystallinity of PA56is slightly higher than PA6 and PA66, which means more regular arrangement of PA56 molecules and explains the higher melting point. Conventional polyamide generally induced a transition towards a pseudo hexagonal unit cell, which transition can be easily observed by X -ray diffraction pattern since the two strong equatorial reflections characteristic of the sheet structure gradually merge by increasing temperature into a single reflection. This temperature is called Brill transition temperature. There have been a lot of studies about Brill transition reported, but lack of a widely accepted explanation for varieties of assumptions. The studies by Laura et al. figured that Brill transition of polyamide56is irreversible caused by increased mobility of polyethylene and bring no damage on hydrogen in the shift process.

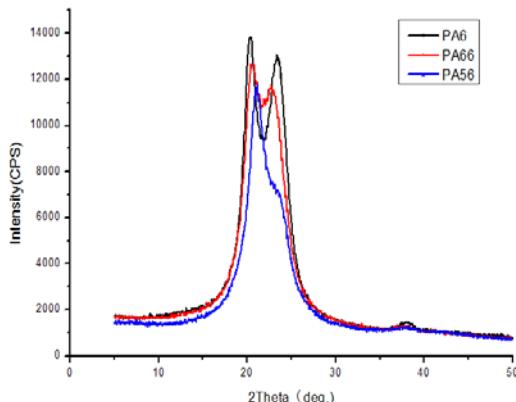


Fig. 4. XRD curves of different polyamidefibers

Conclusion

This study showed that the bio-based PA56 can be spined smoothly under the experimental spinning conditions. The molecular weight comparative study indicated a narrow distribution of molecular weight of polyamide56, which is in good agreement with the result of XRD test that indicated the degree of crystallinity of PA56 is slightly higher than PA6 and PA66. The higher the degree of crystallinity, the higher fiber strength and more stable viscosity which is beneficial for spinning. The structure of PA6, PA66 and bio-based PA56 were investigated by IR curves analysis. Experimental results show that the melting point of bio-based PA56 is 254.1°C which is higher than that of PA6 and PA66, and thermal decomposition temperature is 403.7°C which is slightly lower than that of PA6 and PA66. The results indicate that bio-based PA56 fiber has good heat resistance property and could be applied in high temperature environment. All in all, research of novel bio-based polyamide56 reported is much limited. The bio-based polyamide56 is widely applied in many fields because of its excellent properties.

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