Preparation and characterizations of flame retardant polyamide 66 fiber

Y Y Li[1], K Liu[1] and R Xiao[1,2]

[1]State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, People's Republic of China

Email: xiaoru@dhu.edu.cn

Abstract. The polyamide 66 (PA66) is one of the most important thermoplastic materials, but it has the drawback of flammability. So the flame retardant PA66 was prepared by condensation polymerization using nylon salt and DOPO-based flame retardant in this paper. Then the flame retardant PA66 fiber was manufactured via melt spinning. The properties of flame retardant PA66 and flame retardant PA66 fiber were investigated by relative viscosity, differential scanning calorimetry (DSC), tensile test, vertical burning test (UL94) and limiting oxygen index (LOI) test. Although the loading of the DOPO-based flame retardant decreased the molecular weight, the melting temperature, the crystallinity and the mechanical properties of flame retardant PA66, the flame retardancy properties improved. The flame retardant PA66 loaded with 5.5 wt% of DOPO-based flame retardant can achieve a UL94 V-0 rating with a LOI value of 32.9%. The tenacity at break decreased from 4.51 cN·dtex^{-1} for PA66 fiber to 2.82 cN·dtex^{-1} for flame retardant PA66 fiber which still satisfied the requirements for fabrics. The flame retardant PA66 fiber expanded the application of PA66 materials which had a broad developing prospect.

1. Introduction

Polyamide 66 (PA66) is one of the thermoplastic materials widely used in manufacture of plastics, films, fibers and textiles due to its excellent mechanical properties and chemical resistance[1-5]. However, the limiting oxygen index (LOI) is 24.2% which limits its applications. Thus the flame retardancy has become a necessary requirement for PA66[6-8]. DOPO-based flame retardant is a kind of environmentally friendly flame retardant containing the phosphorus linking pendent group. There have several literatures focused on the DOPO-based flame retardant polyesters and epoxy because of the efficient flame retardancy and low toxic gas evolution during combustion[9-11]. Wang et al[9] prepared 9,10-dihydro-10[2,3-di(hydroxycarbonyl)propyl]-10-phosphaphenanthrene-10-oxide (DDP) and nano α-ZrP flame retardant polyester. The LOI improved from 21.2% to 32.6%, which indicated that the fire retardant performance was significantly improved. However, there hardly any literatures focused on the DOPO-based flame retardant PA66 and PA66 fibers.

In this paper, flame retardant PA66 was prepared by condensation polymerization of nylon salt and DOPO-based flame retardant. Then the flame retardant PA66 fiber was prepared by melt spinning. The properties and characterizations of flame retardant PA66 and flame retardant PA66 fiber were investigated by relative viscosity, differential scanning calorimetry (DSC), tensile test, vertical burning test (UL94) and LOI test.

2. Experimental details

2.1. Preparation of flame retardant PA66 and flame retardant PA66 fiber
Flame retardant PA66 samples were prepared in a GSH-5L polymerization autoclave. At the start of the polymerization, 1500 g nylon salt, 82.5 g DOPO-based flame retardant, 27.5 g hexamethylene diamine (HMDA) and 1000 g deionized water were charged into the autoclave. Then the mixture was heated to 210°C and the pressure was kept at 1.75 MPa. Then the reactor was gradually decompressed to atmosphere pressure and the temperature was heated to 270°C. Then the polymerization was kept at -0.1 MPa at 275°C. Finally, the product was removed from the autoclave and cut into chips.

The PA66 and flame retardant PA66 pellets were dried at 120°C for 48 h under vacuum before melt spinning process. The fibers were prepared using a spinner instrument equipped with a spinneret containing 36 orifices, whose diameter was 0.3 mm. The fibers were collected at a take-up velocity of 600 m·min^{-1}. Finally, the fibers were drawn at a draw ratio of 3.5.

2.2. Characterizations
The relative viscosity was measured at a concentration of 0.01 g·mL^{-1} in H_2SO_4 with an Ubbelohde viscometer at 20°C. The DSC measurements were carried out on a TA Q20 instrument. The samples were heated to 320°C at 40 °C·min^{-1} and remaining at this temperature for 5 min to eliminate the thermal prehistory. Then the samples were cooled to 100°C with a rate of 10 °C·min^{-1} and heated again to 320°C at the same rate. The vertical burning test was conducted according to ASTM D3801-2010 and the LOI test was measured according to ASTM D-2863. The mechanical properties of flame retardant PA66 fiber were carried out at room temperature with a drawing speed of 40 mm·min^{-1} and a clamping distance of 20 mm. Orientation tests were taken using a sound velocity measuring instrument under a tension of 0.1 g·dtex^{-1} at the speed of sound propagation of 20 cm and 40 cm, respectively.

3. Results and discussion

3.1. Molecular weight
It can be seen from Table 1 that the addition of DOPO-based flame retardant had an effect of lowering the molecular weight. The molecular weight decreased from $1.87×10^4$ g·mol^{-1} for PA66 to $0.92×10^4$ g·mol^{-1} for flame retardant PA66. The reason was the incorporation of DOPO-based flame retardant held back the polymerization of PA66 chains and the relative viscosity decreased.

Table 1. The molecular weight of PA66 and flame retardant PA66.

Samples	$\overline{M_\eta}$ (g·mol^{-1})	Relative viscosity
PA66	$1.87×10^4$	2.80
flame retardant PA66	$0.92×10^4$	2.12

3.2. Thermal transitions and crystallinity
In order to study the thermal transitions and crystallinity of PA66 and flame retardant PA66, DSC measurement was carried out. The DSC heating curves and cooling curves of PA66 and flame retardant PA66 are shown in Figure 1. The related DSC results are summarized in Table 2. According to the DSC curves, the melting temperature (T_m) of flame retardant PA66 was lower than that of PA66. The crystallization temperature (T_c) of flame retardant PA66 was detected at 208.59°C which was also lower than that of PA66. Besides, the crystallinity decreased from 33.70% for PA66 to 23.73% for flame retardant PA66. These phenomena were due to the incorporation of the DOPO-based flame retardant to the polymerization system of nylon salt. The DOPO-based flame retardant destroyed the regularity of PA66 main chain, decreased the molecular weight of PA66 and disturbed the

intermolecular interaction of PA66, which caused the reduction of the intermolecular interaction between PA66 molecules and resulting in a lowering of T_m, T_c and the crystallinity[12].
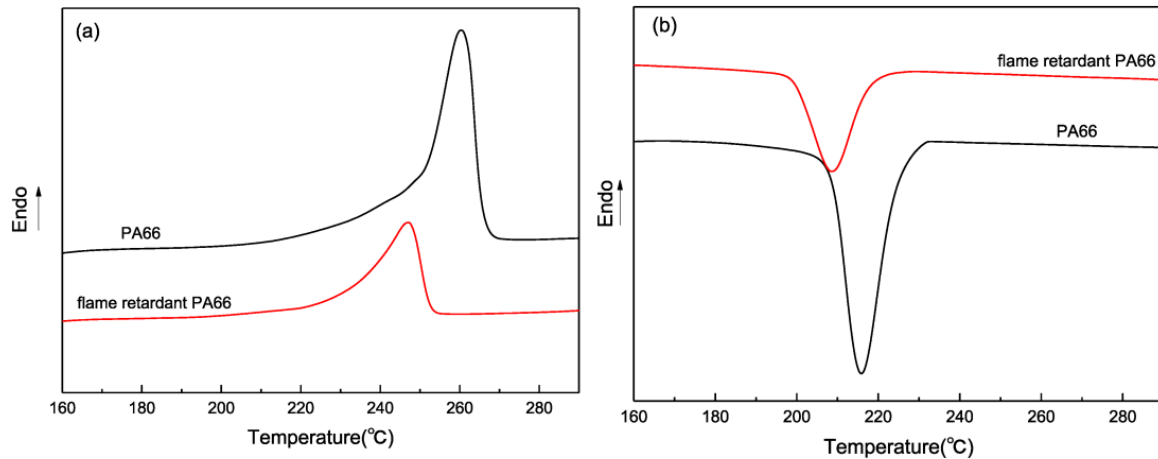

Figure 1. DSC heating curves (a) and cooling curves (b) of PA66 and flame retardant PA66.

Table 2. The DSC results of PA66 and flame retardant PA66.

Samples	T_m (°C)	ΔH_m (J·g⁻¹)	T_c (°C)	Crystallinity (%)
PA66	260.43	65.71	215.87	33.70
flame retardant PA66	247.01	46.27	208.59	23.73

3.3. Flame retardancy properties

The vertical burning test and LOI test are widely accepted as important tests for determining flammability. It can be observed that PA66 showed bad flame retardancy properties. There existed many melt drippings during combustion which can burn the cotton and achieved a V-2 rating in the vertical burning test. As the incorporation of the DOPO-based flame retardant, the self-extinguishing time after ignition and the melt drippings of flame retardant PA66 decreased obviously. The vertical burning test result of flame retardant PA66 with 5.5 wt% of additives achieved a V-0 rating because it showed hardly any melt drippings and the cotton couldn't be ignited. The improvement of the flame retardancy of flame retardant PA66 can also be observed from the LOI test. The LOI value of flame retardant PA66 increased from 24.2% to 32.9%, which was higher than 28% and reached the standard "hard to burn". It was worth nothing that DOPO-based flame retardant made a great contribution to improve the flame retardancy properties of PA66.

Table 3. The vertical burning test and LOI test results of PA66 and flame retardant PA66.

Samples	Vertical burning test		LOI value (%)
	Whether the cotton be ignited	Rating	
PA66	Yes	V-2	24.2
flame retardant PA66	No	V-0	32.9

3.4. Mechanical properties of flame retardant PA66 fiber

As can be seen in Table 4, both the tenacity at break and elongation at break of flame retardant PA66 fiber decreased compared with PA66 fiber, which was inevitable in obtaining flame retardant fibers.

When the content of flame retardant was 5.5 wt%, the strength of the flame retardant PA66 fiber still attained 2.82 cN·dtex^{-1}, which satisfied the requirements for fabrics. The decrease of the mechanical properties of flame retardant PA66 fiber was due to the decrease of the molecular weight and the crystallinity[13].

Table 4. The mechanical properties of PA66 fiber and flame retardant PA66 fiber.

Samples	Tenacity at break (cN·dtex^{-1})	Elongation at break (%)
PA66 fiber	4.51	51.37
flame retardant PA66 fiber	2.82	33.04

3.5. Orientation of flame retardant PA66 fiber

The degree of orientation was represented by orientation factor, which reflects the level of molecular chains arranged parallel to their direction of the preferred orientation unit for reference. Compared with the PA66 fiber, the sound velocity, orientation factor and modulus of flame retardant PA66 fiber decreased. The reason is mainly due to the incorporation of DOPO-based flame retardant, which lowered the molecular weight and the crystallinity, resulting in an attenuation of the sound waves. In addition, the regularity of the PA66 chains was broken up by the presence of the flame retardant, which went against to the axial alignment of the macromolecules in the fibers and affected the propagation velocity of sound waves between PA66 chains, resulting in the decrease of sound velocity, orientation factor and modulus of flame retardant PA66 fiber.

Table 5. The orientation test results of PA66 fiber and flame retardant PA66 fiber.

Samples	Sound velocity (km·s^{-1})	Orientation factor	Modulus (gf·d^{-1})
PA66 fiber	2.29	0.66	59.26
flame retardant PA66 fiber	2.12	0.60	50.79

4. Conclusions

The flame retardant PA66 and flame retardant PA66 fiber was prepared by condensation polymerization using nylon salt. Although the presence of DOPO-based flame retardant decreased the molecular weight, the melt temperature, the crystallinity and the mechanical properties of PA66, the flame retardancy properties improved. The flame retardant PA66 can achieve a V-0 rating according to the UL94 criterion with a LOI value of 32.9%, which showed that the flame retardant PA66 had relatively satisfactory flame retardancy. The breaking strength, elongation break, sound velocity, orientation factor and modulus of flame retardant PA66 fiber decreased compared to PA66 fiber. The tenacity at break of flame retardant PA66 fiber still attained 2.82 cN·dtex^{-1}, which satisfied the requirements for fabrics.

References

[1]   Huang X, Li B, Shi B and Li L 2008 *Polymer* **49** 1049-55
[2]   Bai Y, Huang L, Huang T, Long J and Zhou Y 2013 *Polymer* **54** 4171-6
[3]   Peng J, Walsh P J, Sabo R C, Turng L S and Clemons C M 2016 *Polymer* **84** 158-66
[4]   Xiao J, Tan Y, Song Y and Zheng Q 2016 *RSC Adv.* **6** 41392-403
[5]   Sha K, Hu Y L, Wang Y H and Xiao R 2014 *Mater. Res. Innovations* **18** S4-843-S4-7
[6]   Jimenez M, Duquesne S and Bourbigot S 2013 *Polym. Degrad. Stabil.* **98** 1378-88
[7]   Naik A D, Fontaine G, Samyn F, Delva X, Louisy J, Bellayer S, Bourgeois Y and Bourbigot S

2014 *RSC Adv.* **4** 18406-18

[8]   Zhan Z, Xu M and Li B 2015 *Polym. Degrad. Stabil.* **117** 66-74

[9]   Wang D Y, Liu X Q, Wang J S, Wang Y Z, Stec A A and Hull T R 2009 *Polym. Degrad. Stabil.* **94** 544-9

[10]   Hamciuc C, Serbezeanu D, Carja I D, Vlad-Bubulac T, Musteata V E, Forrat Pérez V, Guillem López C and López Buendia A M 2013 *J. Mater. Sci.* **48** 8520-9

[11]   Liu Y L, Wu C S, Chiu Y S and Ho W H 2003 *J. Polym. Sci.: Polym. Chem.* **41** 2354-67

[12]   Kumar R and Sekhon S S 2013 *Ionics.* **19** 1627-35

[13]   Li Y, Lin Y, Sha K and Xiao R 2017 *Text. Res. J.* **87** 561-9