

인과 황을 포함하는 폴리아마이드 난연제의 합성과 나일론 직물에 적용

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(2016년 7월 20일 접수, 2017년 4월 26일 수정, 2017년 9월 17일 채택)

Synthesis and Application of a Polyamide-containing Phosphorous and Sulfur Flame-retardant for Nylon Fabric

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(Received July 20, 2016; Revised April 26, 2017; Accepted September 17, 2017)

Abstract: Monomer of polyamide (PA66) and flame-retardant intermediate product (FR) were firstly synthesized, and the flame-retardant (PA-FR) was further gained by polymerization of PA66 and FR. The structure of PA-FR was confirmed by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), X-ray photoelectron spectroscopy (XPS), and gel permeation chromatography (GPC). The thermal properties of PA-FR and the finished fabric were evaluated by thermal gravity analysis (TGA) and differential scanning calorimetry (DSC). Moreover, X-ray diffraction analysis (XRD) showed that melting eutectic reaction occurred between PA-FR and nylon fabric. The experimental results showed that the limiting oxygen index (LOI) value of PA-FR treated fabric and PA-FR treated fabric after 10 laundries were improved to 28.8% and 26.4%, respectively. It implied that PA-FR had a good and durable function of imparting fire-resistance to nylon fabric.

Keywords: nylon fabric, flame-retardant, synthesis, flame-retardant finishing, eutectic.

Introduction

Nylon is one of the polymers most used for synthetic fibers.¹ In comparison with other fibers, nylon fiber has many advantages, such as good abrasion resistance, good moisture absorbency, high elastic resilience, high breaking strength, high ductility, excellent dyeing properties and low specific gravity, etc.^{2,3} But its thermal performance is very poor, nylon fabric is easy to combust and produce melt dripping. Those shortcomings seriously limit extensive application of nylon. So, it is vital for nylon fabric to be endowed with durable flame-retardancy.

Currently, there are three technical approaches to make flame-retardant nylon. First, flame-retardant nylon can be produced by copolymerization using phosphorus-containing diamine monomers, but it has not achieved commercial suc-

cess; Second, another way is to add flame-retardant additives to nylon polymers during fiber spinning; At last, flame-retardant finishing has been considered as a practical way to produce flame-retardant nylon fabrics.⁴⁻⁹ However, mostly used flame-retardants are halogen and formaldehyde flame-retardant system, which is harmful to the environment and human.^{10,11} Moreover, due to the special structure of nylon fabric, common flame-retardant is difficult to be combined with nylon fabric, resulting in poor washability of treated nylon fabric, and it is often accompanied with the application of cross-linker, while it has a bad effect on handle of fabrics.

In order to solve these problems above, we carried out studies in an effort to synthesize a new durable flame-retardant containing phosphorus and sulfur for nylon fabric. When the flame-retardant was heated, phosphate groups degraded to form phosphoric acid and make nylon cellulose change into phosphorylated cellulose, then they further decomposed to form residue (char and phosphorus oxides). At the same time, sulfur element could reduce the melting point of nylon fabric

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and eutectic reaction occurred between PA-FR and polyamide chain segments of nylon fabric. And the durability of this retardant system to multiple laundries was studied to conclude that it is promoted to be a durable flame-retardant. Moreover, it has no free-formaldehyde or halogen and good prospect.

Experimental

Materials. The nylon fabric with a weight of 165 g/m² was supplied by Chenghang Group (Suzhou, China). Adipic acid, hexamethylene diamine, phosphoric acid and thiourea, and anhydrous alcohol (used as solvent for hexamethylene diamine), and sodium hypophosphite (used as catalyst in the reaction process of PA66), and *N,N*-dimethylformamide (DMF, used as solvent for thiourea), dicyclohexylcarbodiimide (DCC, used as dehydrating agent in the reaction process of PA-FR), and ammonia (used to adjust pH) were all AR grade chemicals supplied by Sinopharm Chemical Reagent Company Limited.

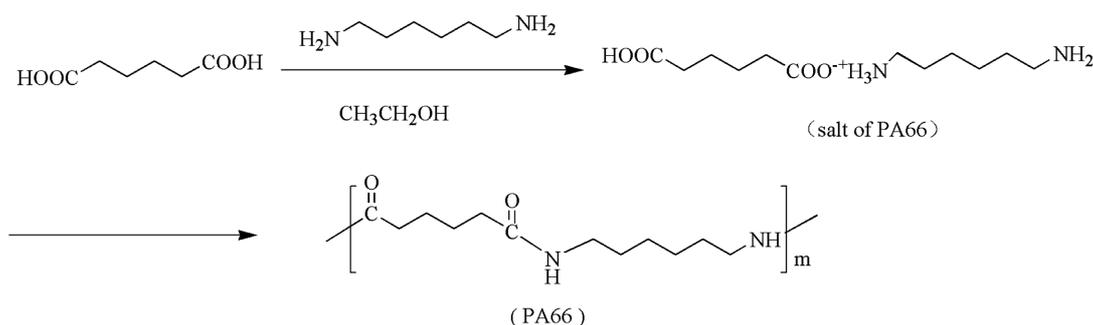
Synthesis Process of the Flame-Retardant.

Synthesis of PA66: PA66 was synthesized using adipic acid and hexamethylene diamine, with minor adaptations, the method of Carothers *et al.*¹² Adipic acid (8.76 g, 0.06 mol) was first put into a 100 mL four-necked flask equipped with agitator and thermometer. Deionized water used as solvent was put into the flask, and the flask was heated to make adipic acid dissolved at the temperature of 55 °C. Hexamethylene diamine (7.66 g, 0.066 mol) dissolved in anhydrous alcohol was added into the reaction vessel while the agitator was stirring fast.

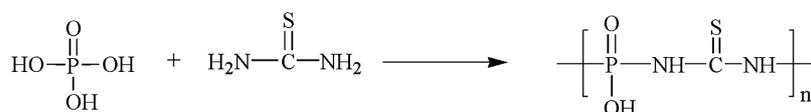
After the addition of hexamethylene diamine was completed, the temperature of reaction system held about 55 °C for 2 h. Then, deionized water and unreacted materials were removed under reduced pressure. The product was washed with anhydrous alcohol, and PA66 salt was kept in a vacuum desiccator. Next, PA66 salt and sodium hypophosphite used as catalyst and little hexamethylene diamine were put into the flask. The four-necked flask was depressurized and heated to 180~230 °C for 4 h. Finally PA66 was obtained. The reaction process of PA66 was shown in Scheme 1. FTIR (KBr, cm⁻¹): 3400 and 3070 (N-H), 2890 and 779 (-CH₂-), 1689 (C=O), 1520 (CO-NH).

Synthesis of FR: Thiourea (11.40 g, 0.15 mol) and DMF used as solvent were put into a four-necked flask equipped with an agitator, a thermometer and a condenser tube. Phosphoric acid (14.85 g, 0.15 mol) was added slowly into the reaction vessel. After the addition of phosphoric acid was completed, the temperature of reaction system gradually went up to 80 °C and was kept for 4 h, then DMF was removed under reduced pressure, and the product was washed with anhydrous alcohol. The reaction process of FR was shown in Scheme 2.

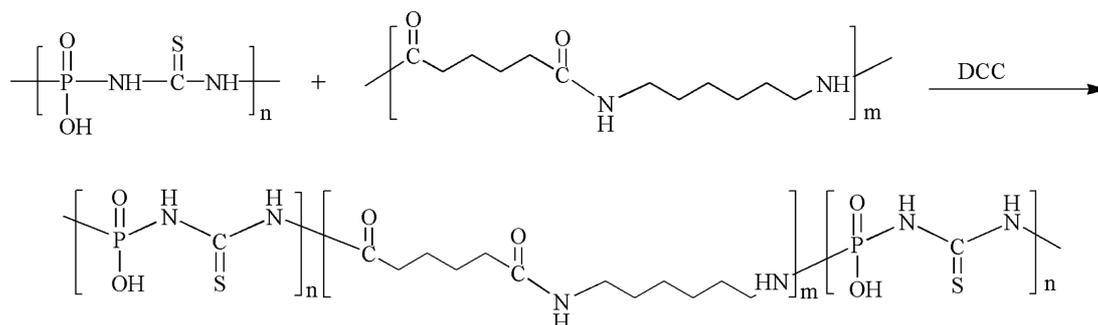
Synthesis of PA-FR: PA66 (10 g) and FR (6 g) were added into a four-necked flask equipped with an agitator, a thermometer, a condenser tube and a tube with N₂. A certain amount of DCC used as dehydrating agent was added into the flask while the agitator was stirring fast. The temperature of reaction mixture gradually went up to 110 °C and was kept for a certain time. Then product was soaked in anhydrous alcohol



Scheme 1. Reaction process of PA66.



Scheme 2. Reaction process of FR.



Scheme 3. Reaction process of PA-FR.

for 24 h and dried. Finally, the product was adjusted to the required solid content by deionized water, and the pH was adjusted with ammonia. Finally PA-FR was obtained. The reaction process of PA-FR was shown in Scheme 3.

Fabric Treatment Procedure. Fabric samples (30 × 20 cm) were dipped in finishing solution which contained 200 g/L of the flame-retardant for 1 min and then padded on a two roll padding mangle at a fixed pressure. The wet pickup was about 90 % after two dips, two nips. Then the fabric was dried on a heat-setting stenter at 110 °C for 1 min, and then cured at 150 °C for 3 min. Then, the cured fabrics were soaked in water containing soap flakes 2 g/L at 60 °C for 20 min, then rinsed with tap water and then dried at 105 °C for 2 h.

Characterization. FTIR were recorded on the NICOLET 5700 infrared spectrometer (Thermo Nicolet Corporation, USA) with a scanning number of 30 using KBr pellets. ¹H NMR were recorded on a 400 MHz (Bruker Varian, Switzerland) using dimethyl-d₆ sulfoxide (DMSO-d₆) as solvent. Detailed element information was obtained by XPS, using a PHI-5400 spectrometer. Molecular weight and molecular distribution determined via GPC, known as size exclusion chromatography (SEC). The GPC instrument consists of LC-20AD pump and equipped with RID-10A refractive index detector. Distilled water was used as elution solvent. TGA was performed on a Diamond TG/DTA instrument (Perkin-Elmer International AG, USA). All samples for TG were measured from 25 to 600 °C at a heating rate of 10 °C/min with a continuous nitrogen, and sample's weight was in the range of 0-10 mg. Differential Scanning Calorimetry (DSC) analyses were performed under a 50 mL/min nitrogen gas flow using a DSC Q100 from thermal analysis instruments with scanning rates ranging from 0.08 to 0.33 K s⁻¹, and all samples weight were in the range of 2-6 mg. Pyrolysis gas-chromatography mass-spectrometry (PY-GC/MS) was carried out on a system combined with a FRONTIER PY-2020iD Pyrolyser and a

SHIMADZU GC/MS QP2010. The smoke density test was measured on the FTT0064 smoke density box (Fire Testing Technology Corporation, UK), fabric samples were 8×8 cm², radiation power was 25 kw/m², and heating temperature was 569 °C. Micro-scale combustion calorimeter (MCC) test was measured on the FTT0001 (Fire Testing Technology, UK) according to "Method A" of ASTM D7309-2007 at a heating rate of 1 °C/s. All experiments were conducted in triplicate. Flame-retardant properties (char length, continue burning time, smoldering time) were determined according to the GB/T 5455-2014. Grade B1: char length is less than or equal to 15 cm, continue burning time is less than or equal to 5 s, smoldering time is less than or equal to 5 s; Grade B2: char length is less than or equal to 20 cm, continue burning time is less than or equal to 10 s, smoldering time is less than or equal to 10 s. Limiting oxygen index (LOI) tests were measured on a HC-2 analyzer (Jiangning Analyzer Instrument Company, China) with strips of nylon fabrics according to the GB/T 5454-1997. The test fabric was clamped vertically in the center of the combustion chamber and ignited by a butane burner with a mixture of oxygen and nitrogen continuously going through with a flow rate of 171 mL/min. XRD was measured on X Pert-Pro MPD diffractometer. The conditions for test were as follows: copper target (λ=0.154 nm); voltage was 40 Kv; electric current was 35 mA; and the range of 2θ was 5°-45°. The breaking strength of fabrics was measured on a LFY-201D electrical fabric strength tester according to the GB/T 3923.1-1997. The whiteness of fabrics was measured according to GB/T 8424.2-2001 on a WSB-2 whiteness meter.

Results and Discussion

Chemical Composition and Structure Analysis. FTIR spectra of FR and PA-FR were shown in Figure 1. Observing curve 1, the characteristic peaks at 1465, 1405, 1087 and

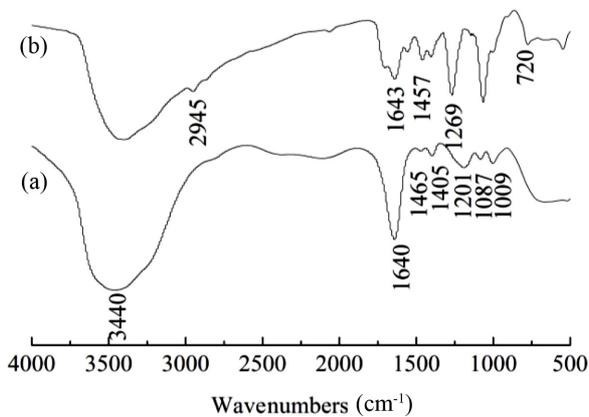


Figure 1. Infrared spectra of (a) FR; (b) PA-FR.

1009 cm^{-1} corresponded to $-\text{C}=\text{S}$, $\text{C}-\text{N}$, $\text{P}-\text{N}-\text{C}$ and $\text{P}-\text{O}$ groups, respectively. The characteristic peak at 3440 cm^{-1} was the absorption overlap of $\text{P}-\text{N}$ and $\text{P}-\text{OH}$, and the strong band in 1640 and 1201 cm^{-1} was $\text{N}-\text{H}$ deformation vibration and $\text{P}=\text{O}$ stretching vibration. The spectroscopic evidences were matched to the structure of FR. Compared with that in curve 1, the target product had new characteristic absorption peak in curve 2. The different characteristic bands at 2945, 1701, 778, and 1269 cm^{-1} corresponded to $-\text{CH}_2$, $-\text{C}=\text{O}$, $-\text{CH}_2$ and $\text{P}=\text{O}$ groups, respectively. These results implied that FR had been reacted with PA-66, and PA-FR was obtained successfully.

A detailed structural analysis and absolute conformation of the conversion were shown in Figure 2. It could be found that the typical peak of $\text{DMSO}-d_6$ was observed at 2.49 ppm. The peaks of PA66 at δ 1.57, δ 2.18, δ 3.05, δ 2.65 and δ 1.55 corresponded to $-\text{CH}_2\text{CH}_2\text{CO}$, $-\text{CH}_2\text{CH}_2\text{CO}$, $-\text{CONH}$, $-\text{NCH}_2\text{CH}_2$, and $-\text{NCH}_2\text{CH}_2$, respectively. The peak of FR at δ 2.0 and δ 3.01 corresponded to $\text{P}-\text{NH}-\text{C}$ and $\text{NH}-\text{C}=\text{S}$. And the characteristic peaks of PA-FR at δ 3.37, δ 2.21, δ 2.78 and δ 2.07 corresponded to $\text{S}=\text{C}-\text{NH}-\text{COCH}_2$, $\text{S}=\text{C}-\text{NH}-\text{COCH}_2$, $-\text{CH}_2\text{NH}-\text{P}$ and $-\text{CH}_2\text{NH}-\text{P}$, respectively. The results of ^1H NMR stated that the target product was obtained successfully. In addition, the composition of PA66 and FR units in PA-FR was 33:17 calculated from the ^1H NMR spectrum.

XPS Analysis of FR. The elements on FR were investigated by XPS. The element spectra were shown in Figure 3. In 283 and 530 eV, there were strong peaks, which were C1s and O1s absorption peaks, respectively. In 128, 162 and 397 eV, the peaks were P 2p, S 2p and N 1s absorption peaks, respectively. The result was consistent with that of FR.

GPC Analysis of PA-FR. Molecular weight and molecular weight distribution of PA-FR were shown in Figure 4. It could

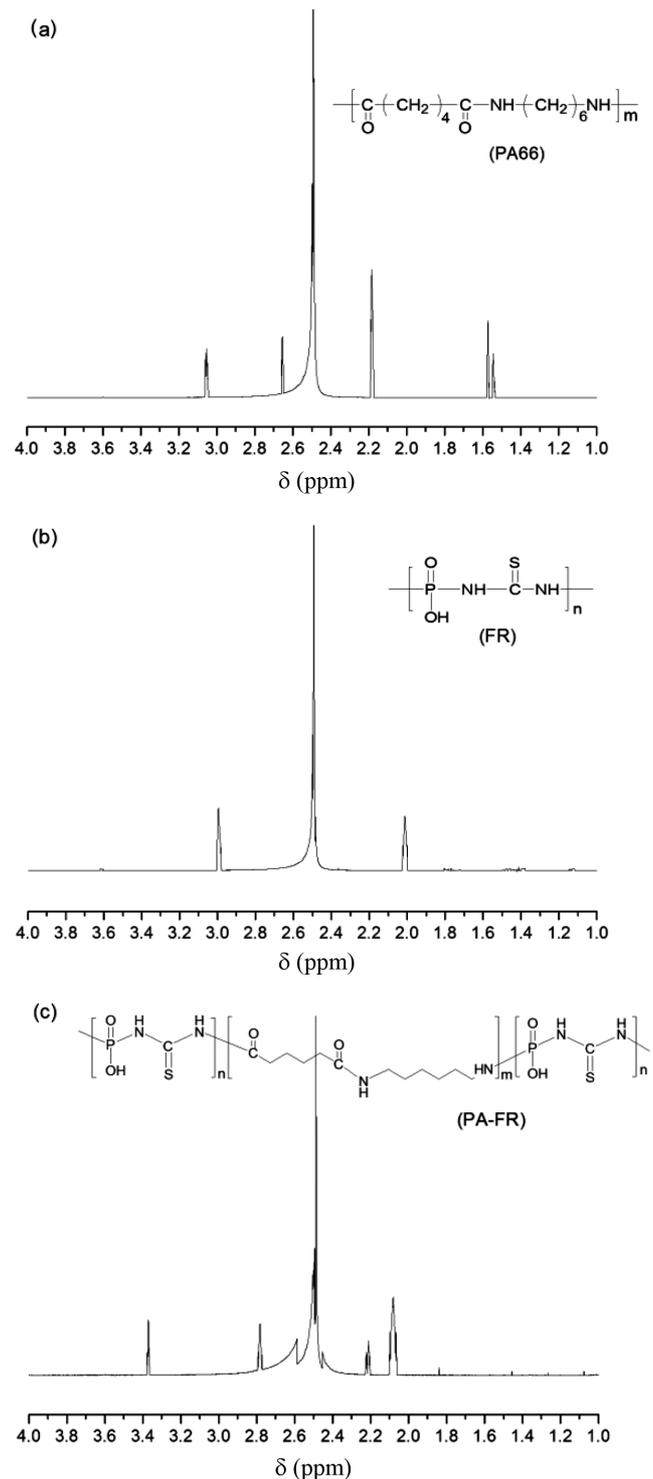


Figure 2. ^1H NMR spectrum of (a) PA66; (b) FR; (c) PA-FR.

be found that number-average molecular weight (M_n) and weight-average molecular weight (M_w) of PA-FR were 20500 and 30200, respectively, and polydispersity index (PDI) is

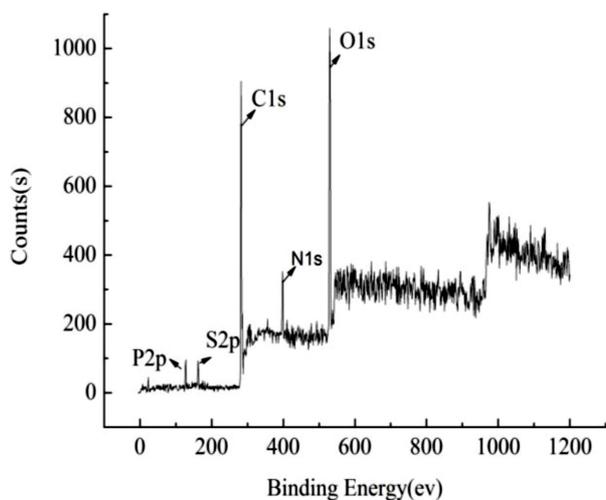


Figure 3. XPS analysis of FR.

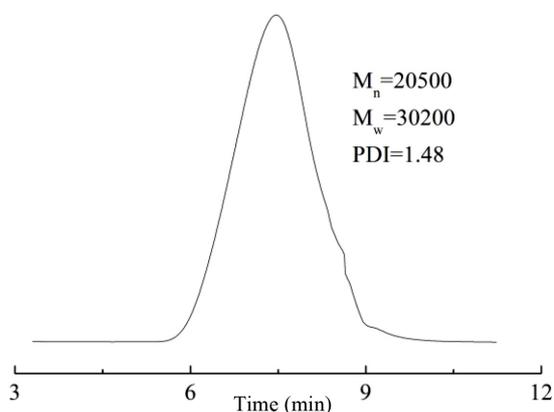


Figure 4. GPC analysis of PA-FR.

about 1.48. The result indicated that molecular weight distribution of the PA-FR was concentrated.

Thermal Properties of PA-FR. The TG-DTA thermograms of PA-FR are shown in Figure 5. From the TG and DTA in Figure 5, the pyrolysis of PA-FR consisted of three stages. In the first stage, the weight loss was about 5% at the temperature below 200 °C that resulted from the heat absorption of water evaporation and the decomposition of oligomers in PA-FR, which corresponded to the curve b showing an endothermic peak at about 100 °C. The second stage occurred at the temperature range from 200 to 370 °C with the weight loss of 80%, corresponding to the curve b showing a strong exothermic peak at 360 °C. In this stage, the weight loss was very significant and fast, because of the rapid decomposition of the effective constituents in PA-FR. Nucleophilic reaction occurred between sulfur decomposed from PA-FR and polyamide chain, which led to rupture of the polyamide macromolecular chain.

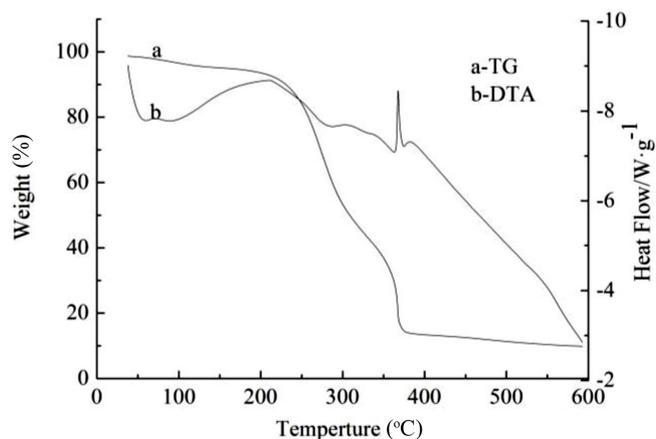


Figure 5. TG-DTA of PA-FR.

And the decomposed phosphorus formed volatile glutinous compounds, covering the surface of nylon fabrics to isolate oxygen and heat.¹³⁻¹⁶ Besides, chain scissions of aliphatic amide degraded to form NH_3 , CO_2 , N_2 , etc.,¹⁷ diluting the concentration of combustible gas in the air. In the third stage, the weight loss was about 5% at the temperature range from 370 to 600 °C, and the mass fraction was only 10% at 600 °C.

PY-GC/MS Analysis. The significant pyrolysis compounds of PA-FR were listed Table 1. It was reported that phosphorus and sulfur element could generate stable compounds to cover the surface and form a carbon layer to block the further diffusion of oxygen and heat at the reaction zone, meanwhile it also blocked the diffusion of volatile combustible compounds to flame. It was noticed that the compounds containing phosphorous and sulfur atoms were not detected in the pyrolysis product, which indicated that they still remained in the residue. The PY-GC/MS analysis revealed degradation behavior of PA-FR, showing that the residue contain phosphorous and sulfur.

TG Analysis of Nylon Fabric. The thermal decomposition of nylon fabric was investigated by TGA in the atmosphere of nitrogen.^{18,19} TGA curves of the nylon fabric were shown in Figure 6. It could be seen that the initial decomposition temperature of the untreated nylon fabric and PA-FR treated nylon fabric started at 360 and 220 °C, respectively. The solid residue contents of the above-mentioned fabrics were 1.6 and 19.0%, respectively. The results indicated that PA-FR lowered the onset of main decomposition of nylon fabric and increase in solid residue. The main pyrolysis stage showed that PA-FR decomposed before nylon fabric and the effective constituent released from PA-FR prevented nylon fabric from combusting in the temperature range from 200 to 370 °C. Because the

phosphorous of PA-FR degraded to form polyphosphoric acid leading to the dehydration of nylon fabric, and they covered the surface of the fiber and generated a cover layer.^{20,21} In addition, PA-FR also degraded to form sulfur atom which may react with amine end-groups or carboxylic acid end-groups, or attack polyamide linkage by nucleophilic reaction. Then, the

Table 1. Types and Relative Peak Intensity of Pyrolyzed Products from PA-FR

Time (min)	Molecular formula	Molecular structure	Relative peak intensity (%)
1.647	CO ₂ etc.	<chem>O=C=O</chem>	0.36
2.345	C ₃ H ₉ NO	<chem>CC(C)NO</chem>	2.32
6.132	C ₆ H ₉ N	<chem>CC=CC#N</chem>	15.98
7.087	C ₈ H ₁₄	<chem>CC=CC(C)C=C</chem>	4.43
11.253	C ₇ H ₁₀ N ₂	<chem>CC#NCC#N</chem>	2.45
13.556	C ₆ H ₁₁ NO	<chem>O=C1CCCCCN1</chem>	60.90
17.219	C ₁₂ H ₂₃ NO	<chem>O=C1CCCCCCCCCN1</chem>	13.56

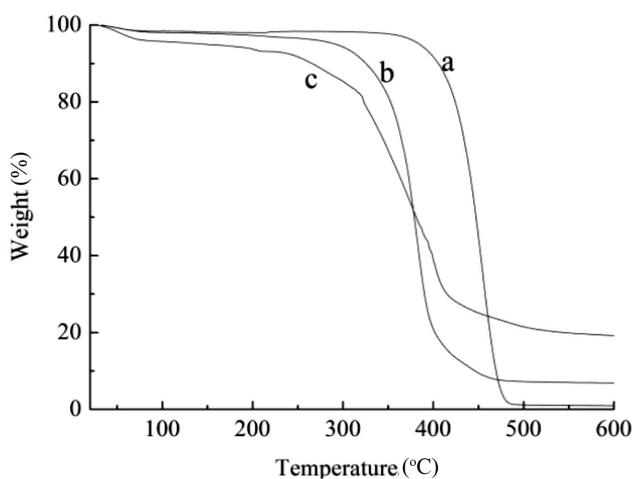


Figure 6. TG curves of (a) the untreated nylon fabric; (b) PA-FR treated nylon fabric after 10 laundrings; (c) PA-FR treated nylon fabric.

phosphorous, nitrogen and sulfur in PA-FR decomposed volatile glutinous compounds forming a layer membranous substance on the surface of nylon fabric at high temperature, which could prevent oxygen from separating to reaction zero and isolate the contact between fire and nylon fabric. So, PA-FR was an effective flame-retardant for nylon fabric. In addition, the initial decomposition temperature and solid residue content of PA-FR treated nylon fabric after 10 laundry cycles were 260 °C and 8.6%, respectively. Although the effect was lower than that of PA-FR treated nylon fabric, it was superior to the untreated nylon fabric. The results indicated that PA-FR had some durable flame resistance.

Smoke Density Analysis. The primary cause of death on the fire hazard is smoke, and the greater smoke density of the material is, the more dangerous firefighting is. It could be seen from Figures 7 and 8 that the highest smoke densities of the untreated nylon fabric and PA-FR treated nylon fabric were 67.45 and 56.54%, respectively. And the untreated nylon fabric and PA-FR treated nylon fabric reached maximum smoke density at 1100 and 900 s, respectively. Because of the rapid decomposition of PA-FR on the nylon fabric, the smoke density of PA-FR treated nylon fabric rose lower than that of the untreated nylon fabric, and the total smoke release was also lower than that of the untreated nylon fabric. When the PA-FR applied, the compact carbon layers were formed on the surface of the nylon fabric, which inhibited the combustion and decomposition of the nylon fabric effectively. Thus, the smoke density of the nylon fabric was decreased. The results meant that PA-FR could effectively decreased the smoke release rate and the total smoke release when nylon fabric was combusting, and PA-FR played an important role in fire rescue.

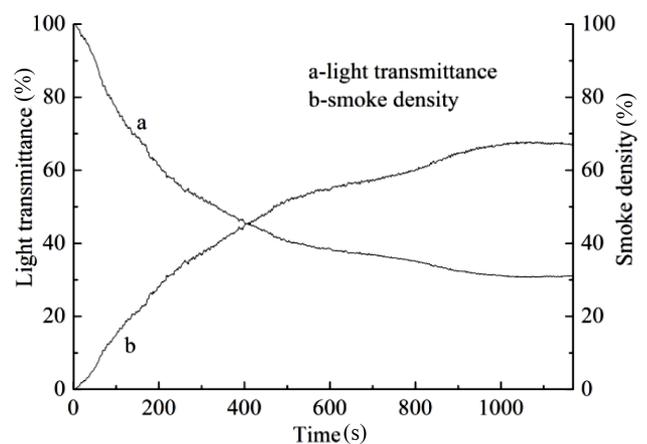


Figure 7. Light transmittance and smoke density of nylon fabric before flame-retardant finishing.

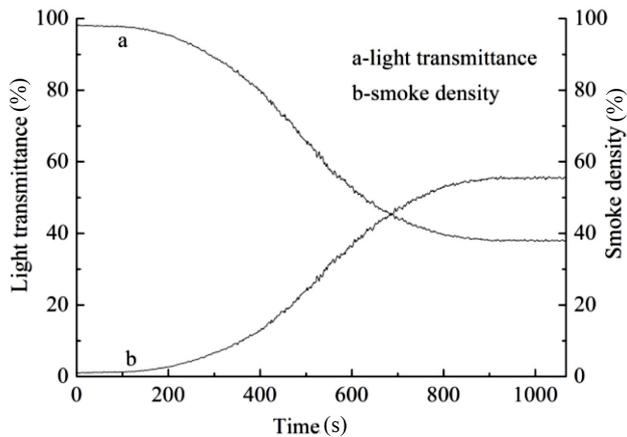


Figure 8. Light transmittance and smoke density of nylon fabric after flame-retardant finishing.

Micro Combustion Calorimeter Analysis. The heat release rate (HRR) of the untreated nylon fabric, PA-FR treated nylon fabric, PA-FR treated fabric after 10 launderings and PA-FR were measured using pyrolysis combustion flow calorimetry (PCFC). The values of the heat release capacity (HRC), the peaks of heat release rate (pHRR), total heat release (THR), and the temperature at pHRR (T_{pHRR}) were shown in Table 2. Figure 9 showed HRR of nylon fabrics. It could be seen that

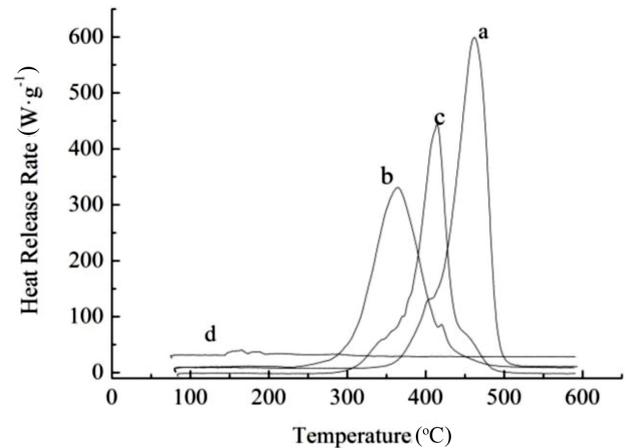


Figure 9. Heat release rate of (a) the untreated fabric; (b) PA-FR treated fabric; (c) PA-FR treated fabric after 10 launderings; (d) PA-FR.

HRR of the untreated nylon fabric reached a maximum of 580.8 W/g when the temperature was at 459.6 °C, and THR was 30.3 kJ/g. The decomposition was ended at 520 °C with 1.36 % of the original weight as char yield. Compared with the untreated nylon fabric, pHRR, THR, and T_{pHRR} of PA-FR treated fabric were decreased to 309.7 W/g, 23.0 kJ/g and 362.3 °C, respectively, and the char yield was increased from

Table 2. Micro-scale Combustion Data of the Untreated Fabric, PA-FR Treated Fabric, PA-FR Treated Fabric after 10 Launderings and PA-FR

Sample	Times	HRC (J/g · k)	pHRR (W/g)	THR (kJ/g)	T_{pHRR} (°C)	Char yield (%)
Untreated fabric	1	572.0	570.4	29.7	457.7	1.45
	2	591.0	589.0	31.3	461.8	1.23
	3	577.0	583.1	30.0	459.3	1.40
	\bar{X}	580.0	580.8	30.3	459.6	1.36
	δ	8.32	7.76	0.69	1.69	0.09
PA-FR treated fabric	1	298.0	299.0	22.5	355.9	12.63
	2	318.0	319.4	23.9	367.4	12.26
	3	309.0	310.7	22.6	363.6	12.45
	\bar{X}	308.3	309.7	23.0	362.3	12.45
	δ	8.18	8.36	0.64	4.78	0.15
PA-FR treated fabric after 10 launderings	1	408.0	404.2	26.4	417.3	10.02
	2	423.0	425.7	27.3	421.6	9.75
	3	429.0	434.2	28.0	416.7	9.33
	\bar{X}	420.0	421.4	27.2	418.5	9.70
	δ	8.83	12.62	1.14	2.18	0.28
PA-FR	1	43.0	37.4	4.1	172.4	9.13
	2	52.0	44.3	4.8	175.9	8.56
	3	47.0	38.1	4.4	180.3	8.86
	\bar{X}	47.3	39.3	4.4	176.2	8.85
	δ	3.68	3.16	0.29	3.23	0.23

1.36 to 12.45%. When the treated fabric was washed 10 times, pHRR, THR, and T_{pHRR} were reached to 421.4 W/g, 27.2 kJ/g, 418.5 °C and the char yield was reached to 9.70%. The MCC data clearly demonstrated that PA-FR could effectively restrained heat release. In other words, that PA-FR applied as a flame-retardant for nylon fabric could effectively lowered the heat release rate of nylon fabric. Although pHRR, THR, and T_{pHRR} of PA-FR treated nylon fabric after 10 laundings were higher than those of PA-FR treated nylon fabric, they were lower than those of the untreated nylon fabric. It indicated that PA-FR was a durable flame-retardant for nylon fabric. For PA-FR, the thermal decomposition started at approximately 155 °C, HRR reached a maximum of 39.3 W/g when the temperature was at 176.2 °C, and THR was 4.4 kJ/g. It could be found that HRC and THR of PA-FR were little when they were compared with those of the untreated fabric.

Relative Crystallinity and Melting Temperature Analysis.

It is well known that X-ray diffraction technology can characterize polymers. In the role of X-ray, the amorphous region of polymer generates continuous shadow, and the crystalline region could generate diffraction line. So, we could evaluate the crystallinity of polymer by XRD. The X-ray diffraction of the untreated nylon fabric and PA-FR treated nylon fabric were shown in Figure 10. Observing Figure 10, it was easily to find that the major X-ray diffraction peak of the untreated nylon fabric appeared when diffraction angle was 22.4°, and a small X-ray diffraction peak appeared at 36.8°. There were a few X-ray diffraction peak appeared at 19.7°, 21.4°, 23.9°, 37.8°, respectively, when the nylon fabric was finished by PA-FR. Compared with the untreated nylon fabric, the intensity of diffraction peak of PA-FR treated nylon fabric decreased obviously, the major peak of PA-FR treated nylon fabric was divided into new peaks, and the half peak width of diffraction of PA-FR treated nylon fabric broaden. So the crystallinity of PA-FR treated nylon fabric was lower than that of the untreated nylon fabric. Because hydrogen bond density of PA-FR was lower than that of nylon fiber and the poor regularity structure to decrease the crystallinity of the finished nylon fiber. In theory, the polyamide chain of PA-FR formed eutectic reaction with amide chain of nylon fiber, when the finished nylon fabric was baking, and the mechanism was consistent with similar compatibility principle. It was concluded that eutectic reaction occurred between PA-FR and nylon fiber.

The DSC curves of nylon fabric and PA-FR treated nylon fabric were shown in Figure 11. It could be found that the melting point of PA-FR treated nylon fabric was lower than

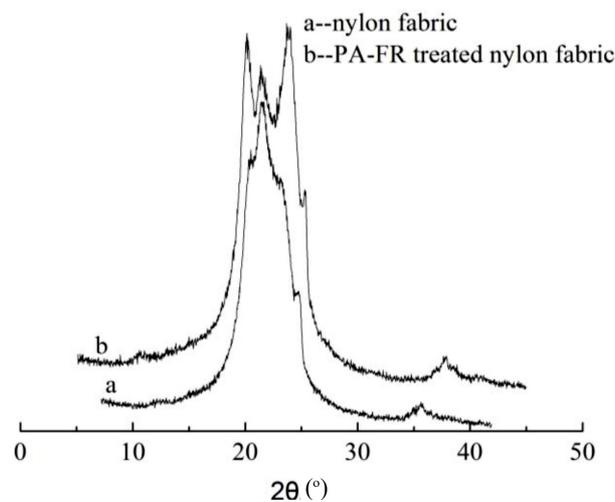


Figure 10. The X-ray diffraction of (a) the untreated nylon fabric; (b) PA-FR treated nylon fabric.

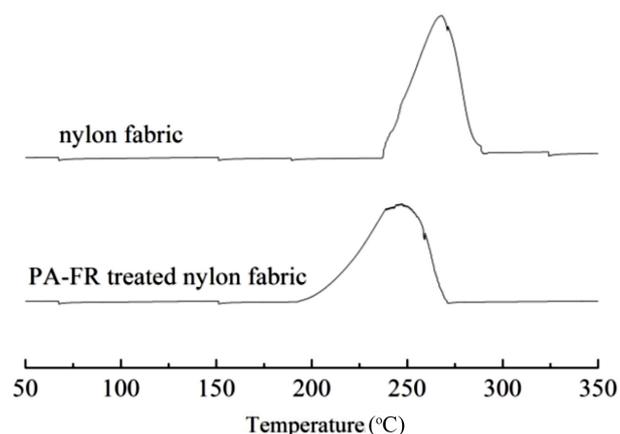


Figure 11. DSC analysis of nylon fabric and PA-FR treated nylon fabric.

that of nylon fabric, resulting from that the hydrogen bond density of nylon fabric was damaged.

Physical and Flammability Performance of PA-FR Treated Nylon Fabric. The results of physical and flammability performance were shown in Table 3. It could be found that the untreated nylon fabric had no flame resistance and the LOI value and damaged carbon length of the untreated nylon fabric were 21.2% and BEL, respectively. In comparison, the LOI value and damaged carbon length of the PA-FR treated nylon fabric were 28.8% and 5.8 cm, respectively. The result indicated that the flame resistance of nylon fabric treated by PA-FR was improved sharply. After 10 laundings, the LOI value and damaged carbon length of PA-FR treated nylon fabric were 26.4% and 7.1 cm, respectively. This indicated that

Table 3. Physical and Flammability Performance of the Untreated Nylon Fabric, PA-FR Treated Nylon Fabric and PA-FR Treated Nylon Fabric after 10 Launderings

Samples	The untreated fabric	PA-FR treated fabric	PA-FR treated fabric after 10 launderings
LOI (%)	21.2	28.8	26.4
Length of charred-fabric (cm)	BEL ^a	5.8	7.1
Continue burning time (s)	- ^b	3.2	5.0
Smoldering time (s)	-	0	0
Whiteness (%)	80.4	75.3	77.1
Tensile strength (N)	620.0	576.3	570.6

^aBurns entire length. ^bBurns all the time.

the finished fabric received a considerable improvement in flame resistance, and it dropped a little after 10 launderings. In addition, the whiteness and tensile strength of PA-FR treated nylon fabric changed slightly. This should be attributed to that eutectic reaction occurred between the same amide chain of PA-FR and nylon fabric at the high baking temperature, so PA-FR could be adhered to nylon fabric. And the sulfur in the flame-retardant could react with carboxylic acid end-groups or amine end-groups of the polyamide, leading to the decrease in the melting point and rapid drip burning of nylon fabric. The nylon fabric was divorced from the heat source or the combustion source and the combustion was suppressed.

Conclusions

On the basis of our study, the following conclusions can be made. The flame-retardant (PA-FR) containing phosphorus and sulfur was a reactive retardant, which was synthesized with adipic acid, hexamethylene diamine, phosphoric acid and thiourea as raw materials. The thermal properties of PA-FR and the finished fabric were evaluated by TGA and DSC. XRD showed that melting eutectic reaction occurred between PA-FR and nylon fabric. And the sulfur in PA-FR played a crucial role in decreasing flammability by nucleophilic reaction with polyamide chain through the analysis of flame-retardant mechanism, and decreased the melting point of finished nylon fabric. When PA-FR was applied to flame-retardant finishing for nylon fabric, the experimental results showed that treated nylon fabric had good and durable flame resistance with the LOI value of 28.8% and the damaged carbon length of 5.8 cm. After 10 launderings, the LOI value was still good (LOI was 26.4% and the damaged carbon length was 7.1 cm). Thus, the PA-FR has the potential to become a practical flame-retardant

for nylon fabric to reduce the flammability, and the flame-retardant finishing system is environmental as it is formaldehyde-free and without halogen.

Acknowledgment: This study was supported by the National Natural Science Foundation of China (NO. 21474070/B040107). The authors would like to thank X. Dong and G. L. Zhou for conducting the MCC and thermal analysis tests.

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