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SYNTHESIS OF SULFUR-CONTAINING NITROGEN AND PHOSPHORUS FLAME RETARDANT AND ITS APPLICATION TO POLYACRYLONITRILE FIBER

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ABSTRACT

Flame retardant ditrimethylolpropane diphosphothiourea (DDT) was synthesized by using ditrimethylolpropane(DTMP), phosphoryl chloride(POCl3) and thiourea as raw materials. Preparation of finishing agent with ethanol as solvent and used as a flame retardtant for polyacrylonitrile fiber. The effect of finishing agent solution concentration, curing temperature and curing time on flame retardancy, whiteness and breaking strength of polyacrylonitrile fiber was also discussed. The optimal synthesis conditions for DDT were determined: the finishing liquid concentration was 200g/L and baking 80°C for 3 min. The results showed that the flame-retardant efficiency reached national standard B1 level and retained higher breaking strength and whiteness.

KEYWORDS

Thiourea, flame retardant, polyacrylonitrile fiber, synthesis process.

1. INTRODUCTION

Polyacrylonitrile fiber, also known as polyacrylonitrile fiber, was made of polyacrylonitrile or acrylonitrile over 85% of the copolymer. It has good elasticity, soft hand, good warmth retention, good dyeing, easy to dry, simple nursing, good weather resistance, mould resistance and chemical stability, so it was widely used [1]. As polyacrylonitrile fiber has an incomplete quasicrystal structure and was sensitive to heat, the thermal stability of polyacrylonitrile fiber was poor. In addition, thermal oxidation cracking in the air will produce the pyrogenation products of acrylonitrile, acetonitrile, ammonia and water, and combustible gases, and then promote the combustion [2]. The limit oxygen index (LOI) of polyacrylonitrile fiber was about 18%, which was the lowest in synthetic fiber and was flammable fiber. It was generally considered that the LOI value was above 26% and has a certain flame retardancy. Therefore, it was of great significance to the study of the flame retardancy of acrylic fabric.

Among many kinds of flame retardants, halogen flame retardants have many advantages, such as good flame-retardant effect, less dosage, little impact on the mechanical properties of materials, etc. At present, most of the fire-retardant polyacrylonitrile fiber has been produced by the copolymerization of chlorinated monomers. The flame retardancy of nitrile chlorofibre, and its fabrics was good and the flame-retardant efficiency was lasting. However, the toxic hydrogen chloride gas will be produced during the severe burns, which endangers the health of the human body and pollutes the environment. Therefore, the flame retardant polya- crylonitrile fiber should develop to the halogen-free environment. The intumescent flame retardant (IFRs) of nitrogen and phosphorus was flame retarded by the synergistic effect of acid source, carbon source and gas source. It has the advantages of halogen-free, low smoke, low toxicity and non-corrosive gas [3]. It was an important study direction of halogen free flame retardant. More and more research and application have been obtained. In addition, through the introduction of silicon, boron, sulfur and other elements can significantly improve the flame retardancy of flame retardants [4-10].

Flame retardant ditrimethylolpropane diphosphothiourea (DDT) was synthesized by using ditrimethylolpropane (DTMP), phosphoryl chloride ($POCl_3$) and thiourea as raw materials. The finishing agent was prepared with ethanol as solvent, and the polyacrylonitrile fiber was subjected to flame-retardant finishing. The effects of finishing agent dosage, curing tem- perature and baking time on the flame-retardant efficiency, whiteness and breaking strength of polyacrylonitrile fiber were discussed, and the optimal synthesis conditions for DDT were determined.

2. EXPERIMENTAL

2.1 Materials and Instruments

Fabric material: 23.8×43.5 tex, 0.021 g/cm^2, 440 /10 cm ×230 /10 cm, Acrylic twill.

Chemicals: Ditrimethylolpropane (DTMP) (industrial products,mass fraction> 99.0%, Jihua Group Jilin Alliance of welfare Chemical Factory), Phosphoryl chloride($POCl_3$) (analysis pure, mass fraction > 99.5%, Tianjin Sailboat Chemical Reagent Technology Co., Ltd.), Thiourea (analysis pure, mass fraction > 99.0%, Tianjin Yongda Chemical Reagent Co., Ltd.).
Main equipment:MU-504 Desktop padder (Beijing Textile Machinery EquiEquipment Co., Ltd.), DHG-9108A Baking oven (Shanghai Precision Instrument and Meter Co., Ltd.), WBS Whiteness instrument (Shanghai XinRui Instrument and Meter Co., Ltd.), YG-026T Electronic fabric strength machine (Wenzhou Fangyuan Instrument Co., Ltd.), LFY-601 Vertical woven fabric flame retardant performance tester (Shandong Textile Science Research Institute).

2.2 Synthesis of flame retardants

(1)0.3mol DTMP were added to a 250mL glass flask equipped with a mechanical stirrer, thermometer sensor, and circumference condenser. Turn on the circumference condensate, stir slowly, and 0.9mol of phosphorus oxychloride were added to the glass flask using a constant pressure dropping funnel (About 85 mL), slower to faster, and the control was completed in about 30 minutes. The temperature was raised to 60°C, and the reaction was carried out at a constant temperature for 4 hours (the reaction time was measured from the start of dropwise addition of phosphoryl chloride), a viscous, light -yellow liquid was optained, that was intermediate (I) ditrimethylolpropane diphosphoryl chloride(DDC). Hydrochloric acid was withdrawn in time during the reaction and was absorbed by lye. The vacuum pump was turned on once every 30 min, 1~3 min/time.

(2)In the ice water bath, 30mL of distilled water was added dropwise to the intermediate (I), control the dropping rate to prevent the reaction system from heating up too quickly. After the dropwise addition was completed, the temperature was raised to 70℃, and hydrolyzed for 1.5 to 2.0 h to yield a brown yellow hydrolysate (II) Ditri-methylolpropane bisphosphate (DTB).

(3)The thiourea was added to the hydrolysate (II), stirring up the temperature and con-stant temperature reaction, the light-yellow viscous liquid was obtained. After the heat was taken out, the white or light-yellow viscous substance by static cooling, that was the target product ditrimethylolpropane diphosphothiourea (DDT) (III).

2.3 Process of flame retardant finish

Finishing agent formula: Ethanol was a solvent, and the finishing agent dosage was 50~300g/L. Process: dip finishing (one-dip-one-nip), 50℃, 20min, rolling residual rate (60%~70%)→Pre-drying (80℃, 3min,)→baking (80~120℃, 0~8min)→finished.

2.4 Analysis testing

2.4.1 Flame retardancy

The ethanol was added to 100 g flame retardant and fixed to 400mL, stirring evenly, that was, the dosage of finishing agent was 250 g/L. The polyacrylonitrile fiber cut to dimensions of 30 cm×9 cm was put into a working bath, 20 min impregnated at 50℃, one dip and one rolling, a wet pick up of 60%~70%, and the treated polyacrylonitrile fiber were baking at 80℃ for 5 min. The flame-retardant cloth was obtained.

The cloth clamp was used to fix the fabric in the combustion box, the gas tank was ventilated to the combustion port, the valve was opened, the power supply was opened, the ignition key was opened, and the flame height was stabilized in the position of the baffle above the burner, after the ignition was successful. After the preparation was ready, press the start key to start the timing, the flame controller automatically moves to the bottom of the sample to burn 3s vertically, then returns to the place, and records the continuous burning time and the time of the smoldering of the sample cloth, taking down the polyacrylonitrile fibers by measurement of the burning length, the width of the middle and the bottom width.

2.4.2 Whiteness Test

Reference to standard GB/T8424.2-2001《Textiles-Tests for color fastness-Instrumental ass- essment of relative whiteness》, parallel test 4 times, and average the results.

2.4.3 Breaking Strength Test

Reference to standard GB/T 3923.1-2013《Textiles-Tensile properties of fabrics Part 1: Determination of breaking strength and breaking elongation using the strip method》, parallel test 3 times, and average the results.

2.4.4 Vertical Combustibility Test

Reference to standard GB/T 5455-2014《Textiles-Burning Behaviour-Determination of Burning Length,Afterglow Time and Afterflame Time of Vertically Oriented Specimens》, ignition time was 3s, parallel test 3 times, and average the results.

B1 level: burning length less than 15 cm, Afterflame Time less than 5 s, Afterglow Time less than 5 s;

B2 level: burning length less than 20 cm, Afterflame Time less than 10 s, Afterglow Time less than 10 s.

2.4.5 IR analysis

Used Fourier infrared spectrometer by using KBr pellets, and the scan range was 4000 ~ 400cm^{-1}.

2.4.6 TG analysis

Synchronous thermogravimetric analyzer at a heating rate of 10℃ /min, over the temperature range of 60 ℃ ~ 600℃, under a nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1 Flame retardant finishing process optimization

3.1.1 Dosage of finishing agent

Flame retardants were prepared according to the better conditions determined above and different concentration finishing agents were prepared. The acrylic fabric was treated by padding and baking. The effect of the amount of finishing agent on the flame retardantcy, whiteness and breaking strength of acrylic fabric was investigated at 80℃ for 5 min. The results were shown in Table 1.

Table 1: Effect of finishing agent dosage on flame retardance, whiteness and breaking strength of acrylic fabrics.

Dosage of finishing agent(g/L)	Afterflame Time (s)	Afterglow Time (s)	Damaged Length (cm)	Whiteness	Breaking Strength(N)
0	47.10	0.07	30.0	82.8	1975.3
50	58.31	0.07	30.0	80.6	986.8
100	34.95	0.07	16.0	79.0	983.8
150	29.50	0.07	11.8	79.3	964.6
200	0.98	0.07	5.1	78.5	959.8
250	0.85	0.07	4.8	76.4	949.2
300	0.079	0.07	3.8	76.3	940.2

From table 1, we can see that with the increase of finishing agent dosage, the flame retardance effect of acrylic fabric was obviously improved, and the whiteness and breaking strength are decreasing. Compared with the untreated acrylic fabric, the whiteness of flame retardant polyacrylonitrile fiber decreased slightly, and the breaking strength decreased significantly. When the dosage of the finishing agent reaches 200 g/L and above, the flame-retardant efficiency of polyacrylonitrile fiber can reach B1 level. At the same time, the fabric also has better whiteness and higher breaking strength. Therefore, the optimal dosage of the finishing agent was determined to be 200 g/L.

3.1.2 Baking temperature

The effects of baking temperature on the flame-retardant efficiency, whiteness, and breaking strength of acrylic fabrics were investigated under the conditions of 200 g/L finishing agent, 3 min pre-baking at 80 °C, and 2 min baking at different temperatures. The results are shown in Table 2.

Table 2: Results of baking temperature on flame retardant, breaking strength, whiteness of acrylic fabrics

Baking Temperature (°C)	Afterflame Time (s)	Afterglow Time (s)	Damaged Length (cm)	Whiteness	Breaking Strength(N)
80	0.98	0.07	5.1	78.5	873.1
90	8.41	0.07	6.6	78.8	891.6
100	1.95	0.07	4.9	78.1	918.5
110	3.40	0.07	5.3	78.1	920.7
120	13.34	0.07	9.1	75.5	928.0

From Table 2, it can be seen that with the baking temperature increases, the flame-retardant efficiency of the acrylic fabric becomes worse, the whiteness decreases slightly, and the breaking strength increases. When the baking temperature was 90°C, the acrylic fabric becomes soft, the flame-retardant efficiency was obviously deteriorated, the after flame time was greatly increased, and the damaged char length was increased. The possible reason was that the glass transition temperature of the polyacrylonitrile fiber was about 90°C. At this time, the polyacrylonitrile polymer segment was loosened and the material properties are mutated. Considering comprehensively, the optimal baking temperature was 80 °C.

3.1.3 Baking time

The effects of baking time (total length of time) on the flame-retardant efficiency, whiteness, and breaking strength of acrylic fabrics were investigated under the conditions of 200 g/L of finishing agent and baking temperature of 80°C. The results are shown in Table 3.

Table 3: Results of Baking time on flame retardant, breaking strength, whiteness of cotton fabrics.

Baking Time(min)	Afterflame Time (s)	Afterglow Time (s)	Damaged Length (cm)	Whiteness	Breaking Strength(N)
3	2.13	0.07	4.8	79.1	942.4
5	2.29	0.07	5.3	79.0	934.5
7	2.06	0.07	4.9	79.1	1163.9
9	3.84	0.07	4.9	78.6	1915.5
11	1.38	0.07	4.8	78.5	1974.7

From Table 3, it can be seen that with the extension of the baking time, the flame-retardant efficiency of the acrylic fabric has not changed much, reaching B1 level; the whiteness has not changed significantly; the breaking strength has increased significantly. Considering that the long baking time affects the production efficiency and causes energy waste, the baking time was selected as 3 min.

3.2 TG analysis

Under the condition of 200 g/L of finishing agent and baking at 80 °C for 11 min, flame-retarded polyacrylonitrile fiber was obtained. The untreated polyacrylonitrile fiber and flame-retarded polyacrylonitrile fiber were taken for thermogravimetry under N_2 atmosphere. The TG chart drawn from the test data was shown in Figure 1.

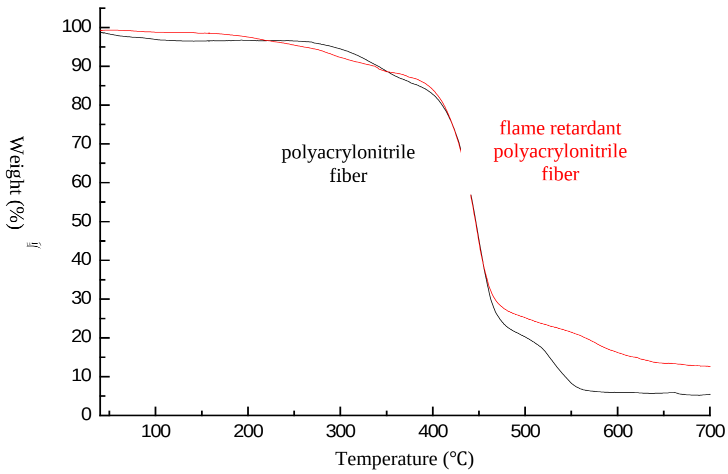

Figure 1: TG curve of ordinary acrylic and flame retardant polyacrylonitrile fiber

From Figure 1, we can see that the initial decomposition temperature, decomposition rate (TG curve slope) and residual carbon content of polyacrylonitrile fiber have significant changes before and after flame retardancy. According to the data of table 4 and Figure 1, it can be seen that the thermal decomposition of the flame retardant polyacrylonitrile fiber was earlier than that of the untreated polyacrylonitrile fiber, and the decomposition rate was slowed down, and the amount of carbon residue was significantly improved.

Table 4: TG curve partial data

Project	Ordinary polyacrylonitrile fiber	Flame retardant polyacrylonitrile fiber
Temperature at 5% weight loss(°C)	337	167
Temperature at 50% weight loss(°C)	429	417
The amount of carbon residue at 500 °C（%）	13.4	17.9
The amount of carbon residue at 700 °C（%）	9.3	15.8

3.3 Comparison of flame retardant efficiency

The untreated polyacrylonitrile fiber and the flame-retardant polyacrylonitrile fiber were respectively subjected to the vertical combustion test, at this time, observe the combustion phenomenon and the combustion effect was compared. The results are shown in Figure 2.

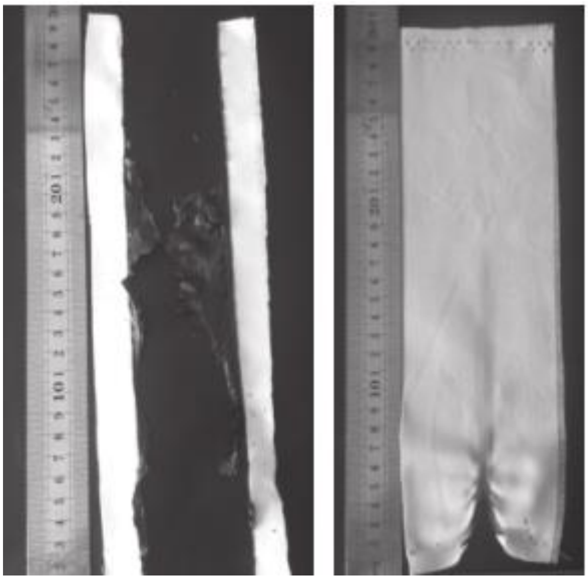

Figure 2: Combustion effect of untreated polyacrylonitrile fiber and flame retardant polyacrylonitrile fiber

It can be seen from Figure 2, the untreated polyacrylonitrile fiber was ignited with the quickly molten and burned, and the flame spread quickly, with a large number of black smoke and blacker residue; after the flame retardant polyacrylonitrile fiber was ignited, the flame was briefly burned and extinguished, the smoke was less, the combustion part had molten, a small amount of black residue, and the flame-retardant efficiency was obvious.

4. SUMMARY

(1) Under the conditions of 200 g/L of finishing agent and 3 min for baking at 80℃, the flame-retardant efficiency of the acrylic fabric can reach the national standard B1, the whiteness of the fabric decreases slightly and the breaking strength decreases obviously, but it still remains at a high value.
(2) TG and combustion tests show that flame retardants have significant Flame Retardancy for polyacrylonitrile fibers from microcosmic and macro perspectives.

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