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STUDY ON THE THERMAL BEHAVIOUR AND FLAMMABILITY OF THE MODIFIED POLYACRYLONITRILE FIBERS

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Abstract

The effects of some kinds of metal ions used as chemical modifications on the thermal properties of the modified polyacrylonitrile (PAN) fibers were studied by DTA, TG, GC and cone calorimetry. The apparent activation energies for the decomposition of the unmodified and modified PAN fibers were determined using Kissinger equation and Broido equation.

Keywords: apparent activation energy, char residue, metal-containing PAN fibers, pyrolysis, thermal analysis, thermal degradation

Introduction

Polyacrylonitrile (PAN) fibers are generally classified as flammable textile material according to their low LOI values [1]. To improve the flame retardation of PAN fibers, the following four ways have been developed during the past decades: (1) post finishing; (2) modification of spinning solution; (3) blending or copolymerisation of polymers; (4) chemical modification. The first three methods have been widely used. However, they are not environmentally friendly methods because of the use of chemicals containing halogen, phosphorus or sulfur. On the contrary, the chemically modified fibers do not contain the above toxic substances. At present, the development of highly efficient and non-toxic flame retardant systems has become a very attractive project in the field of flame retardant techniques. On this account, the study on the chemical modification of PAN fibers has attracted great interest [2–4]. The aim of this work is to study the effect of some metal ions on the behavior of the chemical modified PAN fibers.

Experimental

Materials

Fibers

The lustrous PAN fibers were subjected to modification in the form of wires with linear densities of the elemental fibers of 3.28 dtex, composing of a terpolymer of

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acrylonitrile, methylmethacrylate, and sodium vinylsulphonate, provided by Shanghai Jinshan Chemical Plant.

Reagents

Hydrazine hydrate ($NH_2NH_2 \cdot H_2O$) and metal acetate [$M(II)CH_3COO)_2$, *M*(II)=Cu(II), Zn(II), Mn(II) and Ni(II)] purchased from Beijing Chemical Plant with a purity higher than 98%.

Methods

Sample preparation

The de-oiled PAN fibers were immersed in aqueous solution of hydrazine hydrate (50% by mass) with bath ratio of 1:20. The mixture was heated to 363 K and kept at this temperature for 60 min. The fibers modified with hydrazine were obtained after washing and drying the fibers. Then the fibers were treated with aqueous metal acetate solution (5% by mass) for 30 min at bath ratio 1:20 at 363 K. After washing and drying, the metal-containing modified PAN fibers with good flame retardation were obtained.

LOI value

The LOI value were measured on Stanton Redcroft FTA Instrument according to the method described in the Chinese Standard Method GB 2406-80.

Thermal analysis

TG and DTA were carried out using Shimadzu DT-30 (Shimadzu, Japan) apparatus under the following conditions: sample mass: 4 mg, heating rate: 10 K min^{-1} in static air atmosphere.

Cone calorimetry

Cone calorimeter analysis was carried out on Stanton Redcroft cone calorimeter (PL, England). The operation and test protocols were in accordance with the recommendation in ISO 5660. The specimens for the cone test were prepared by pressing the powdered fiber to form a plate of dimensions 100×100×6 mm. Each specimen was wrapped in aluminium foil and only the upper face was explosed to the radiant heat flux. The incident heat flux was 50 kW m^{-2}. All the specimens were tested in the horizontal orientation.

Pyrolysis gas chromatograph

0.05 g of sample was burned at 1073 K for 3 min. The gas yielded by heating was collected in a bottle using a gas sampling apparatus. 2μl gas sample was injected into the gas chromatograph (Hewlett Packard 4580).

Results and discussion

DTA curves for the unmodified and modified PAN fibers are shown in Fig. 1. The DTA curves in Fig. 1 shows that there are two exothermic peaks for the unmodified fibers. One of the peaks in sharp and appears at about 589 K, which represents the cyclism of the PAN chains by the elimination of HCN [5], and the other is broad and appears in the temperature range of 834–1180 K where the intensive and complete degradation of the fibers takes place [6]. From the DTA curve for the fibers modified by hydrazine, it can be seen that the sharp peak almost disappears and the broad one shifts to the lower temperature range, between 829 and 1047 K. This suggests that the cyano groups in acrylic fibers partly converted to a cyclic crosslinking conjugate structure [2].

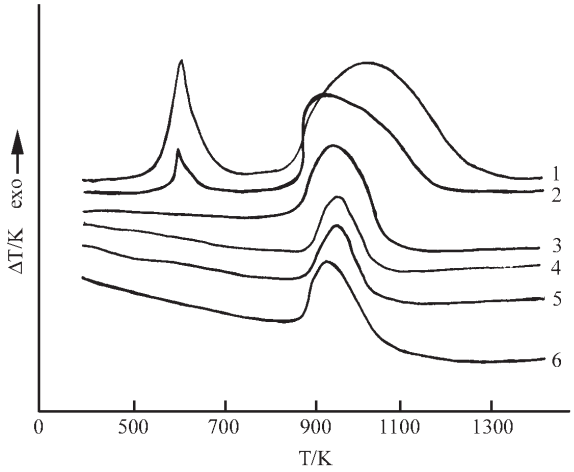

Fig. 1 DTA curves of PAN fibers; 1 – original; 2 – hydrazine modified; 3 – Zn(II)-containing; 4 – Mn(II)-containing; 5 – Cu(II)-containing; 6 – Ni(II)-containing

In comparison with DTA curves the original PAN fibers, the exothermic peak of the complete degradation of the metal-containing fiber shifts toward the low temperature range, and its shape is narrower and sharper, while the original sharp peak disappears completely. The temperature ranges of the complete degradation for the modified fibers containing Cu(II), Zn(II), Mn(II) and Ni(II) are 854–1007, 847–1043, 857–1028 and 852–1038 K, respectively.

The TG curves of the investigated samples are presented in Fig. 2. The thermal degradation of the original PAN fibers is gradual and complete. The thermal degradation of the metal-containing fibers takes place at a higher rate in comparison with the original PAN fibers, but does not comprise the complete degradation of the polymer. The amount of char residue at 1123 K in air and the maximum exothermic peak temperature (T_p) for the original and modified PAN fibers are included in Table 1. The LOI value and the apparent activation energy of thermal degradation for the original

and modified PAN fibers calculated by equation of Kissinger [7] and Broido [8] are also listed in Table 1.

Table 1 Thermal properties of the unmodified and modified fibers

Sample	LOI	T_p/K	E_a/kJ mol^{-1}		Char yield at 1123 K (air)/ mass%
			Kissinger method	Broido method	
Original PAN fibers	18.0	997	155.2	149.8	0
Hydrazine modified	19.0	907	140.6	135.4	0.25
Cu(II)-containing	35	919	105.4	99.7	12.6
Zn(II)-containing	33	932	111.2	103.6	8.9
Mn(II)-containing	32	935	116.8	104.9	8.3
Ni(II)-containing	31	909	115.6	105.7	8.1

Compared with the original fibers and the fibers modified with hydrazine, the amount of the char residue for the metal-containing PAN fibers is much higher, while its activation energy is lower. Some metal oxides can exist in the char residue and their content is up to 45–55% [2, 4]. If we substract the contribution of metal oxides, clearly the char residue for the metal-containing fibers is still much higher than that for the unmodified fiber. The conclusion drawn from these data is in agreement with LOI values as presented in Table 1, i.e., the metal-containing PAN fibers burn at lower rate than the original fibers and the fibers modified with hydrazine.

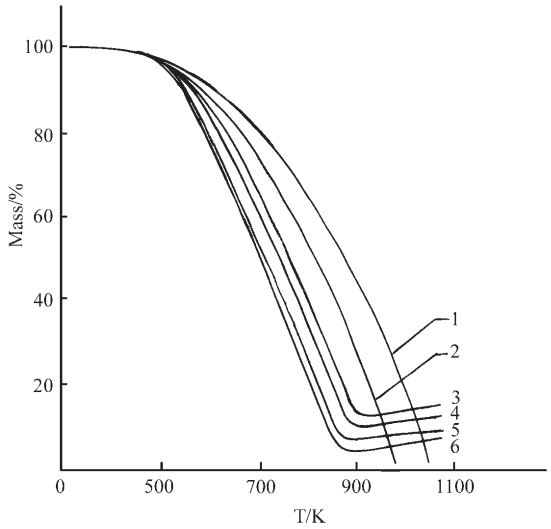

Fig. 2 TG curves of initial and modified PAN fibers; 1 – original; 2 – hydrazine modified; 3 – Zn(II)-containing; 4 – Mn(II)-containing; 5 – Cu(II)-containing; 6 – Ni(II)-containing

As seen in Table 2, the amount of toxic HCN released from the metal-containing fibers is much lower than that from the unmodified fibers on heating. Similarly, the amounts of C_2H_3CN, CH_3CN, CH_4 and C_2H_4 released from the metal-containing fibers are also lower than those from the unmodified fibers. These results suggest that metal-containing fibers can decrease the flammability.

Table 2 The content of the gases released from the heated unmodified and the modified fibers

Sample	Amount of released gas/mg g^{-1} fiber				
	HCN	CH_3CN	C_2H_3CN	CH_4	C_2H_4
Original fibers	195	15	49	3.4	45
Hydrazine modified	27	8.0	5.5	3.3	1.6
Cu(II)-containing	16	0.9	1.3	0.6	5.9
Zn(II)-containing	18	1.0	1.4	0.7	6.6
Mn(II)-containing	18	0.9	1.4	0.8	6.5
Ni(II)-containing	19	1.1	1.3	0.7	6.6

The effect of the metal ions on the heat release rate (HRR) of the PAN fibers is shown in Fig. 3. It can be seen in Fig. 3 that the value of HRR for the modified PAN fibers is low compared with that of the original fibers. In the case of the original PAN fibers the presence of the intensive exotherm peak appeared at 583 K (Fig. 1) leads to a high HRR. The lower HRR for the metal-containing fibers indicates that the metal ions may take part in the cyclisism reaction [9–12]. As the cyclic structures are the precursors for the formation of the residual char structure, it is concluded that metal

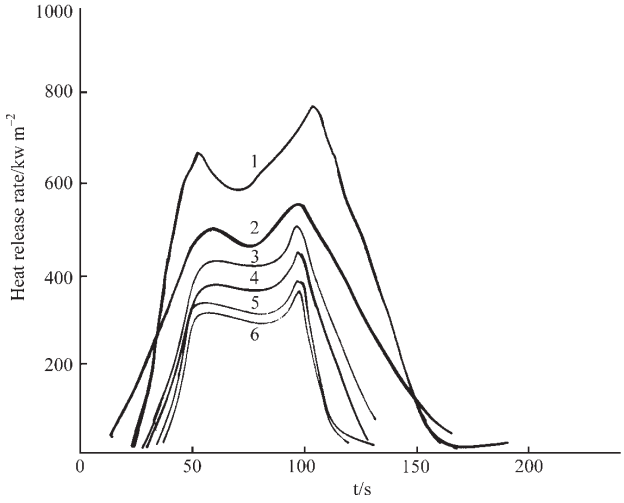

Fig. 3 Effect of metal ions on the heat release rate of PAN fibers at 50 kW m^{-2};
1 – original; 2 – hydrazine modified; 3 – Zn(II)-containing; 4 – Mn(II)-containing; 5 – Cu(II)-containing; 6 – Ni(II)-containing

ions contained in the PAN fibers promote the formation of cyclic structures and char residue. On this account the PAN fibers are imparted with flame retardation after treatment with metal acetate.

The studied fibers are composed of a terpolymer of acrylonitrile, methylmethacrylate and sodium vinylsulphonate. The chemical interaction between the CN-groups of PAN and hydrazine takes place in aqueous medium. The reactions between the CN-groups of the polymer and hydrazine and the changes having occurred in the composition and structure of the fibers, were observed by DTA, gas-chromatographic investigations of the pyrolytic gases. Our observations show that the modification processes change the chemical composition, as well as the chemical parameters of the fibers. The behavior of the modified PAN fibers differs from that of initial fibers (Table 1, Figs 1–3) to a great extent.

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