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RESEARCH ARTICLE

Ming GAO, Rongjie YANG

Synthesis and application of amino resinous intumescent flame retardants

Abstract A kind of amino resinous intumescent flame retardants (IFR) was firstly synthesized, and the structure of the main composition was determined to be a caged bicyclic macromolecule containing phosphorus. The 30% weight of IFR was added into the flexible polyurethane foam (FPUF) to get retardant FPUF which has 26.5% of the limiting oxygen index. The date of CONE show that the heat release, smoke and gas of the flame retardant FPUF are much decreased and the activation energy decreases by 54 $kJ \cdot mol^{-1}$. It shows that the IFR can catalyze decomposition and carbonization of FPUF.

Keywords intumescent flame retardant, flexible polyurethane foam, caged bicyclic macromolecule

Intumescent flame retardant (IFR) without halogenated additives and antimony oxides as main compositions is friendly environmental. Polymer containing IFR having low smoke, low toxicity, low corrosion and no molten dropping during a fire was considered to be originated from the forming a homogeneous char layer, which can isolate the transfer of oxygen and heat between material and flame. So the IFR technology has been one of the hottest topics in research in the flame retardant field, and the IFR is considered as a hopeful way to produce halogen-free flame retardant [1, 2].

However, low compatibility between polymer and low molecular IFR leads to poor mechanical properties, which is hard to use in engineering [3, 4]. At present, the main methods to improve the compatibility are to use cross-linkings agent on IFRs, but the improvement is highly limited, while macromolecular IFR is generally expensive [5].

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Ming GAO (✉), Rongjie YANG
Department of Environmental Engineering, North China Institute of Science & Technology, Beijing 101601, China
E-mail: gaoming@ncist.edu.cn

Therefore, a kind of cheap and effective macromolecular IFR with good compatibility is mainly focused. In this paper, a new amino resinous intumescent flame retardant has been synthesized. Its structure of main composition was determined to be a caged bicyclic macromolecule containing phosphorus. When it was added to flexible polyurethane foam (FPUF) to 30% weight, the obtained flame retardant FPUF will possess 26.5% of the limiting oxygen index, but little effect its mechanical properties. The flame retardancy and thermal degradation behaviors of the flame retardant FPUF were studied by TG and CONE. The decomposition activation energies and the flame retardant mechanism was also discussed.

1 Experiments

1.1 Synthesis of IFR

1.1 mol formaldehyde (37% formalin)was added into aminoethyl alcohol at pH 8 and heated. Then, a mixture of melamine 0.2 mol and urea 0.3 mol with a weight ratio of 4∶2∶1 was added by 3 steps. After the first addition of the mixture, the solution was heated to 90°C for 40 min and the pH was adjusted to 5.2 and then reacted at 80°C to get a solution with a nephelometric point of 40°C. The second part of mixture of melamine and urea then was added. When the nephelometric point of solution reaches to 80°C. The third mixture was added and reacted for 20 min to get melamine-urea-formaldehyde prepolymer (MUF). 85% phosphoric acid 1 mol and pentaerythritol 0.5 mol were mixed, heated to 120°C, stirred for 2–4 h without water distillation to get pentaerythritol diphosphonate. The pentaerythritol diphosphonate was added slowly into MUF, reacted at 90°C for 20 min to get amino resinous intumescent flame retardant (IFR) with a main composition of pentaerythritol diphosphonate melamine \urea\formaldehyde resin salt. The IFR with a content of 7% P, 14% N is a colorless transparent liquid, solidified after 0.5 h, 80.2% of char yield, and 101.5 cm^3/g of intumescence degree at 400°C for 0.5 h.

1.2 Preparation of samples

Using a one-step foaming process, 100 part of polyether polyol (VORANOL 3010), 1.0 part of foam stabilizer (L580), 0.2 part of catalyst (A-33), 2.4 part of foam agent (F-11) and a little of flame retardant were mixed in a high-speed stirrer. Then 38 part of isocyanate (Desrnodur T80) was added and stirred until the mixture became white, then poured into a mold. A. polyurethane specimen was obtained after ripened for 0.5 h at room temperature.

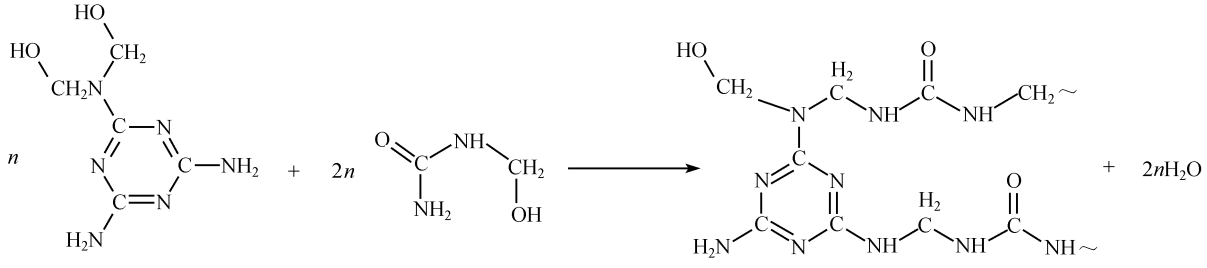
1.3 Analysis of the samples

FPUF Sample containing 30% (weight) flame retardant was used for measurement. The IR spectra were determined on a NEXUS-470 FTIR (Nicolet) spectrophotometer using KBr technology. Limiting oxygen index (LOI) values were determined in accordance with ASTMD-2863 using a sample of 100 mm×6.5 mm×3 mm. CONE data were measured on a Stanton Redcroft Cone Calorimater with a sample of 100 mm×100 mm×40 mm. Thermogravimetry (TG) was carried out on a DT-40 thermal analyzer under a dynamic air (dried) atmosphere at a heating rate of 10°C min^{-1}.

2 Results and discussion

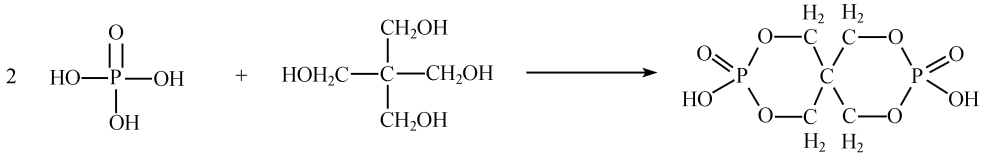
2.1 Synthesis of IFR

(1) Synthesis of MUF



(2) Synthesis of pentaerythritol diphosphonate

IFR was traditionally synthesized using reagents such as methyl cyanide, CH_2Cl_2, CCl_4, and $POCl_3$, then hydrolyzed [6,7]. But the reference method is expensive and not environment friendly. In this paper, the pentaerythritol and phosphoric acid were used to get IFR in water [8].

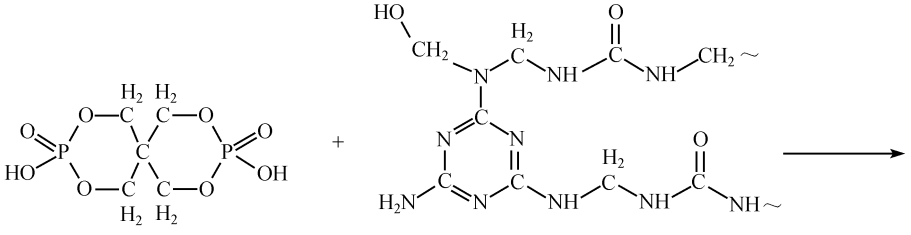


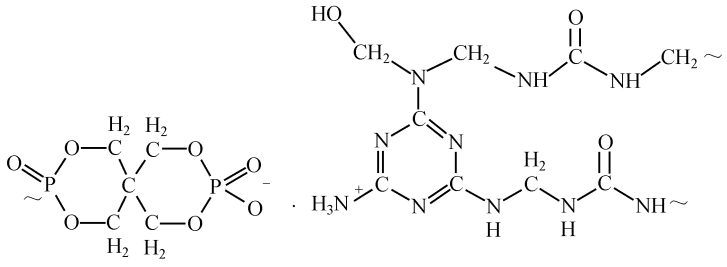
(Pentaerythritol diphosphate)

Other phosphates were formed in the reaction while the pentaerythritol diphosphate is the main composition because of its stable bicyclic structure.

(3) Synthesis of IFR

Pentaerythritol diphosphate and MUF were used to synthesize IFR as follows:





(Pentaerythritol diphosphonate melamine\urea\formaldehyde resin salt)

2.2 IR spectra of IFR

IR (KBr), (cm^{-1}) spectrum of IFR is shown in Fig. 1. The peaks of 2938, 2890 (w, CH_2), 1240–1280 (P=O), 2800–3050 (CH_2), 1024, 877, 780, 677 (dicyclic P–O–C), 3141, 1679 (N–H), 3341 (–OH). This is consistent with the expected structure.

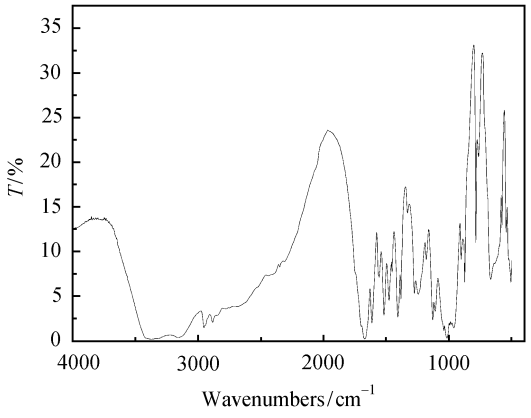


Fig. 1 Fourier transform IR spectra of IFR

2.3 Cone calorimeter

Cone calorimeter was used to evaluate flame retardancy of the samples. The external heat fluxes usually chosen were 30 kW/m^2. The parameters obtained included the rate of heat release (RHR), total heat release (THR), time of ignition (TTI), smoke production rate (SPR), carbon monoxide yield (Y_{CO}) and carbon dioxide yield (Y_{CO_2}) for samples 1–3 are shown in Table 1.

2.3.1 Heat release

The heat release of the combustion process is the key problem in the fire, it directly relates to the combustibility of materials. In this study, the peak heat release rate (RHR peak) and THR were used to evaluate the heat release of samples during the fire. The data is shown in Table 1.

From Table 1, we can see that, RHR_{Peak} of FPUF containing IFR is decreased by 57.12%, which shows that IFR greatly weakened the strength of flame burning, and suppressed the combustion reaction. THR for sample 3 is decreased by 46.26% showing a significant reduction of heat, which leads to an interruption of combustion reaction. The higher LOI (26.5%) also shows its good flame-retardancy. For FPUF containing MUF (sample 2), RHR_{Peak} and THR are also decreased but only a little, which shows limited flame retardancy of the single amino resin. This is supported by its lower LOI. The ignition of samples corresponds to the results of the heat release, *i.e.* an increased TTI for sample 2, and the most difficult to ignite for sample 3.

Fire propagation index (FPI) shows the extent of a fire [9], it is a ratio of TTI and the peak of RHR as follows: $FPI = TTI/RHR_{peak}$.

The greater the FPI is, the better the flame retardancy is. To see Table 1, FPI for sample 3 is 0.53, it is 13 times larger than that of FPUF showing its significant flame retardancy.

2.3.2 Gas and smoke release

Gas and smoke release was determined to be that the smoke production rate (SPR), carbon monoxide yield (Y_{CO}), and carbon dioxide yield (Y_{CO_2}) for samples 1–3 are shown in Table 1.

Table 1 Effect of flame retardants (FR) on combustibility of FPUF

No	FR	RHR_{Peak} /($kW \cdot m^2$)	THR /(MJ/m^2)	TTI /s	FPI	LOI /%	SPR /(m^2/s)	Y_{CO} /%	Y_{CO2} /%
1	—	140.21	56.31	6	0.043	17.5	0.00693	0.0200	1.17
2	MUF	110.30	42.34	18	0.16	21.4	0.00173	0.0268	2.14
3	IFR	60.12	30.26	32	0.53	26.5	0.00123	0.0039	0.41

Table 2 TG parameters of FPUF containing flame retardants

Sample No.	Flame retardant	Stage	Weight loss /%	Temperature range /°C	E_a /(kJ·mol^{-1})	Char. yield /%
		1	5.5	25–250		
1	—	2	73.7	250–390	81.5	0.6
		3	20.2	390–700		
		1	9.3	25–250		
2	MUF	2	61.2	250–380	62.4	2.0
		3	27.5	380–700		
		1	5.3	25–185		
3	IFR	2	52.9	185–373	27.4	11.2
		3	30.6	373–700		

From Table 1 we can see that as compared with FPUF, the SPR for sample containing MUF shows decrease, but Y_{CO} and Y_{CO_2} show increase in some degree. For sample containing IFR, the SPR, Y_{CO} and Y_{CO_2} show much decrease. These results indicate a very good smoke suppression effect of IFR to FPUF.

2.4 Thermogravimetry analysis

Thermogravimetry (TG) curve was carried out under a dynamic air atmosphere from room temperature to 700°C as shown in Fig. 2. The char yields were determined at 700°C from TG curves and the corresponding parameters are given as shown in Table 2.

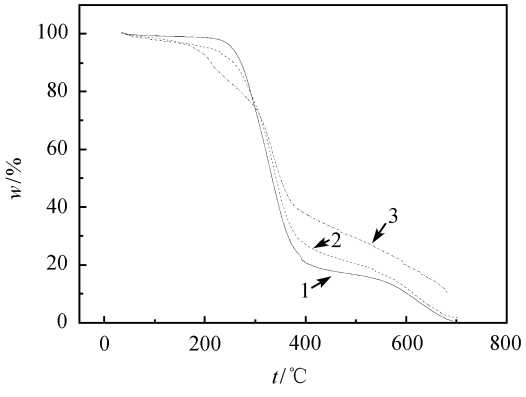


Fig. 2 TG curves of samples (1–3)

The decomposition activity energies of samples were studied by the equation of Kissinger [10]. The equation is represented as follows:

$$\frac{\mathrm{d}\ \ln(\Phi/T_m^2)}{\mathrm{d}(1/T_m)} = \frac{-E\mathrm{a}}{R}$$

where Φ is the rate of temperature increase in K/min (Φ= 2, 5, 10, 20), T_m is the maximum temperature at the peak position in K, E_a is the decomposition activity energy, and R is the gas constant (8.314 J mol^{-1}K^{-1}). From the slope of the plot of $\ln(\Phi/T_m^2)$ versus $1/T_m$, the activation energy Ea can be calculated, *i.e.* $E_a = R \times$ slope.

From Fig. 2 and Table 2, we can see that there is a small effect for MUF on the pyrolysis of FPUF. As compared with the FPUF, the activation energy (62.4 kJ·mol^{-1}) decreases, char yields (2.0%) increases. However, there is still much weight loss in the final stage (600–700°C). For sample 3, there are some obvious differences attributed to flame retardancy in the pyrolysis process: the main stage of pyrolysis is divided into two stages, emergence of a new phase of slow pyrolysis (170–320°C); high char yields of 11.2%, decreased activation energy by 54 kJ·mol^{-1}, which shows that IFR can catalyze decomposition of FPUF, corresponding to the new stage in TG curves. It is suggested that the initial reactions of the flame-retardants containing phosphorus are dephosphorylation and that the released acids, then catalyze the dehydration and carbonization of FPUF [2, 11], resulting in the increasing of thermal stability of FPUF, a short stage of fast pyrolysis and more char yields.

3 Summary and conclusions

In this paper, a kind of amino resinous intumescent flame retardants was firstly synthesized using cheap materials, and their structure of main composition was determined to be a caged bicyclic macromolecule containing phosphorus. The flame retardant role of IFR is that it can catalyze the dehydration and carbonization of FPUF. The activation energy of FPUF containing IFR is decreased by 54 kJ·mol^{-1} compared to FPUF, resulting in more char yields and less combustible gas. The data of CONE show that for FPUF containing IFR, the heat release, smoke, CO and CO_2 are much decreased. FPUF containing 30% weight of IFR gets 26.5% of LOI, which shows that IFR is a good cheap flame retardant.

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