*Bulgarian Chemical Communications, Volume 46, Number 4 (pp. 882 – 886) 2014*

# The effect of flame retardant additives on the combustion performance of flexible polyurethane foam

Chen Yingjie[1*], Liu Zhipeng[1], Dai Peigang[1], Liu Lan[2]

[1]*Guangdong Testing Institute of Product Quality Supervision,510330 Guangzhou, China*

[2]*School of Chemistry and Chemical Engineering Sun Yat-sen University, 510275,Guangzhou, China*

Submitted April 12, 2014

In this work, flexible polyurethane foams (FPUFs) were prepared by a one-step method with different flame retardant additives. Then, the combustion performances of the FPUFs were tested by evaluating their oxygen indices and smoke toxicities (OI) and by cone calorimetry (Cone). The results showed that the flame retardant performances of FPUFs prepared with 10% wt brominated flame retardant and 10% wt triazine triamine phosphate (MPOP) were improved. At an irradiance of 30 kW/m$^2$ with a sample thickness of 50 mm, the peak heat release rates of these two samples were 284.0 Kw/m$^2$ and 270.8 Kw/m$^2$, respectively. However, the smoke toxicity of the former showed greater harmful, and when the FPUF contained more than 4% wt brominated flame retardants, the smoke toxicity reached the WX level.

***Key words*****:** FPUF，Brominated Flame Retardants，Combustion Performance

## INTRODUCTION

Due to accelerated industrialization and urbanization, the market for building materials has undergone dramatic growth in China. Polyurethane (PU) has a special structure and excellent performance, so it has been very extensively used. Meanwhile, because polyurethane (PU) is the product of a polyhydric alcohol compound (R-OH) and isocyanates (RN=C=O), the combustion process releases large amounts of toxic gases. Thus, PU materials incur a high fire risk [1]. Flexible polyurethane foam (FPUF) is a part of the polyurethane molding material with a porous structure and is the most flammable portion of the polyurethane material.

The flammability of FPUF limits its applications in many fields, and therefore, enhancing the flame retardant properties of FPUF would be invaluable [2]. Flame retardants for FPUF include reactive flame retardants and additive flame retardants, defined by the relationship between the flame retardant and the base material. A reactive flame retardant affects the thermal stability, but its use is difficult in industrial production. In contrast, additive flame retardants are easy to use with simple production processes; thus, they have been widely used to date [3]. In this paper, FPUFs were prepared by a one-step method with different foam flame retardant additives. Then, the combustion performances of the FPUFs were tested by evaluating their oxygen indices (OI) and smoke toxicities and by the use of a cone calorimeter (Cone). We have tried to provide a reference work for the appropriate selection of flame retardants.

## TEST

### *Materials*

Polyether glycol (PPG-5623, hydroxyl value of 28.0 KOH mg/g with a degree of functionality of 3, CSPC); polyether polyol (POP CHF-628, hydroxyl value of 28.0 KOH mg/g with a degree of

* To whom all correspondence should be sent. E-mail: jietchen@126.com

functionality of 3, Jiangsu Changhua Polyurethane Science & Technology Co., Ltd); toluene diisocyanate (TDI 80/20, degree of functionality of 3, Shanghai Basf Coating Co., Ltd); dibutyltin dilaurate (PUCAT L-33, Foshan City Puhui New Material Co., Ltd); stannous octoate (YOKE T-9, Jiangsu Yoke Technology Co., Ltd.); niax silicone L-540/STL DR; melamine (BK69 Macro Wei Chemical Co., Ltd); chloroalkyl poly phosphate (RDT-9, Guangzhou Yue Peng Chemical Technology Co., Ltd); 2,2',4',4',5,5-hexabromodiphenyl ether (HBB); 1,1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane (TBECH, J&K Scientific Ltd); triazine triamine phosphate (MPOP, Hefei Fine Collection Institute of Chemical Industry); and deionized water (self-made).

### *Apparatus*

Oxygen index measuring instrument (Fire Testing Technology, FTT); cone calorimeter (Fire Testing Technology, FTT); smoke toxicity test device (Nanjing Shangyuan Fenxi Yiqi CO., LTD); and a mechanical agitator.

### *Preparation of FPUF*

According to the formula found in Table 1, the PPG, POP and deionized water were all combined in a 1000 ml plastic beaker.

**Table 1**. Formalation of FPUF

| Material | Ingredient/g |
|---|---|
| PPG | 75～90 |
| POP | 10～25 |
| TDI 80/20 | 31.5～40 |
| Stannous octoate | 0.2～1.5 |
| Dibutyltin dilaurate | 0.1～0.5 |
| Niax silicone | 0.6～1.0 |
| Flame retardants | 2.0～15.0 |
| Deionized water | 1.8～2.0 |

Dibutyltin dilaurate, niax silicone, stannous octoate and the corresponding flame retardant were then added and stirred with a mechanical mixer for 2 h with the material temperature kept at 25 °C. Finally, TDI 80/20 was added, and the mixture was stirred at high speed for 4 to 5 s and then immediately poured into the natural foaming mold [4] with the temperature maintained at 25 °C for 24 h. The densities of the prepared materials were controlled to be 50 ± 2 kg/m3.

### *Test Method*

Oxygen Index tested According to ISO 4589-2:1996, with test temperature 23±2ºC, humidity at 50 ~ 55 % and sample size 100×10×10 mm.

Heat release rate tested according to ISO 5660-1:20 with irradiance setting at 30kW/$m^2$ and sample size 100×100×50 mm.

Smoke toxicity tested according to GB/T 20285-2006.

## RESULTS

### *Oxygen Index (OI)*

Figure 1 compares the oxygen indices for different flame retardant additives with mass fractions of 10%. Due to the flame retardant properties of POP itself, even without the addition of a flame retardant, the oxygen index of blank FPUF still reached 21.6%. The oxygen index of FPUF with RDT-9 (10%) added was higher than when MA (10%) was added. Phosphorus flame retardants act as a barrier between the air and the combustion products. Chlorine flame retardants work by the radical dilution of the oxygen in the air. Thus, the cooperative effect of these two flame retardant classes can achieve better performance than only MA. Among halogen flame retardants, brominated flame retardants are particularly prominent. The oxygen index reached 24.6% with the addition of HBB (5%) and TBECH (5%). However, the oxygen index achieved by adding MPOP (10%) was the best, reaching 25.2%, which can be attributed to the cooperation of N and P. The charring of the solid phase and the isolation of the air phase achieved a better flame retardant effect.

### *Heat Release Rate (HRR)*

The heat release rate refers to the thermal radiation intensity of presupposition, i.e., the rate of heat release per unit area after ignition in kW/$m^2$. The heat release rate can be divided into the

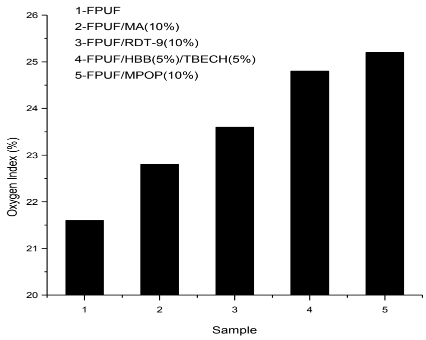


**Fig. 1**. Oxygen index of FPUF adding additive flame retardants.

average heat release rate and the peak heat release rate (pHRR). The average heat release rate has a practical function in the early evaluation of the contribution of the material itself as well as in early flame retardant and fire safety design [5]. The peak heat release rate (pHRR) is one of the most important parameters in evaluating the fire characteristics of materials. An irradiance of 30 kW/m$^2$ approximates actual fire conditions. Therefore, 30 kW/m$^2$ was used in the cone calorimeter test. Figure 2 shows the heat release rate curves of the four specimens at an irradiance of 30 kW/m$^2$. Among them, the heat release rate of blank FPUF reached the highest value. The pHRRs of the FPUFs with RDT-9 and MA additives were more or less the same, and both exceeded 500 kW/m$^2$. Meanwhile, the FPUFs with HBB (5%) and TBECH (5%) additives exhibited a pHRR reduced to 284 kW/m$^2$. The pHRR of the FPUF with the MPOP (10%) additive reached

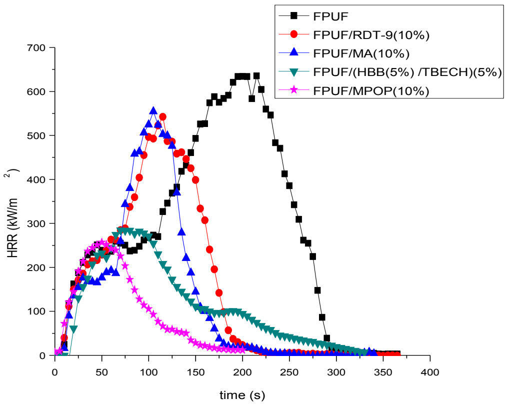


**Fig. 2**. The heat release rate curve of the four specimen in the irradiance of 30kW/m$^2$.

the lowest value, which was 5% lower than for the brominated flame retardant.

*Total Heat Release（THR）*

The total heat release of the cone calorimeter test refers to the total heat release per unit of sample area after complete combustion in MJ/m$^2$. The total heat release is an important parameter for evaluating the thermal hazard of the actual material. The greater the total heat release of the material, the more potential fire danger the material poses. According to Figure 3, the THR of blank FPUF is far greater than for the other four types of FPUFs prepared with flame retardant additives. During the combustion process of FPUF with a MPOP additive, the surface expansion phenomenon was clearly observed. The isolation of the charring increases the effect of the flame retardant, which leads to the minimum total heat release among the tested samples.

*Mass loss rate（MLR）*

The weight sensor supporting the sample pool in the cone calorimeter records the masses automatically. The mass loss rate was

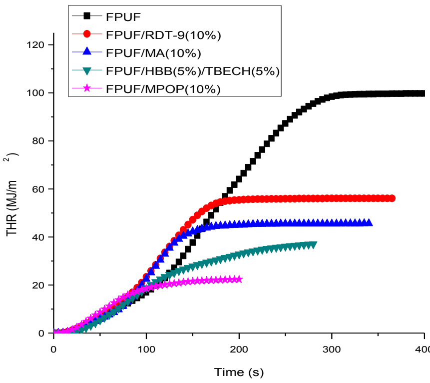


**Fig. 3.** The total heat release curve of the four specimen in the irradiance of 30kW/m$^2$

calculated using the five point finite-difference method. This parameter is closely related to the heat release rate, the ratio of the extinction area and the formation rate of CO. The larger the mass loss rate, the more violent the burning of the sample that occurs. Figure 4 shows the mass loss rate curves of the FPUFs with various flame retardant additives at mass fractions of 10%. Among these samples, the one with the MPOP (10%) additive showed the smallest mass loss rate and thus burned relatively slowly. By observation of the combustion processes of all of the samples, it was found that all of the specimens ignited within 5 s. Furthermore, the entire sample surface participates in the combustion process, resulting in rapid shrinking. The carbonization qualities of the residues after combustion ranged from 3% to 5%. The addition of a flame retardant changes the mass loss rate, but in the high irradiance used in this study, the samples show few differences. The charring rate of FPUF with the MPOP additive is the highest.

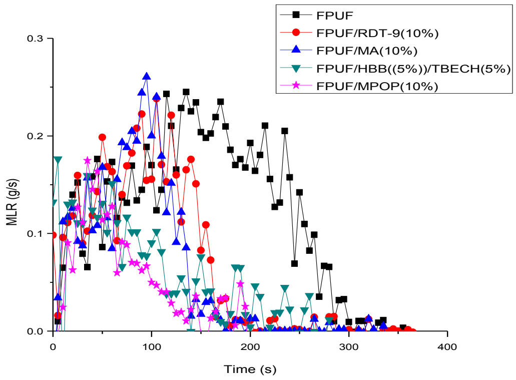


**Fig. 4.** The mass loss rate curve of different of FPUF adding different flame retardants

*Specific extinction area（SEA）*

The specific extinction area refers to the smoke production capacity per mass unit after the decomposition and evaporation of the combustible sample in $m^2$/kg. As shown in Figure 4, the FPUFs with the HBB and TBECH additives demonstrate strong smoke producing abilities due to incomplete combustion. This phenomenon demonstrates the smoke hazard from the use of brominated flame retardants, which pose high health risks to humans[6]. The FPUF with a MPOP additive produced less smoke, showing its ideal flame retardancy.

*Smoke toxicity*

The same materials in the same smoke concentrations show maximum toxicities under the conditions of no flame and complete smoke production. For each material, we tested the animal toxicity under the above conditions. The smoke concentration when the experimental animals reach the test

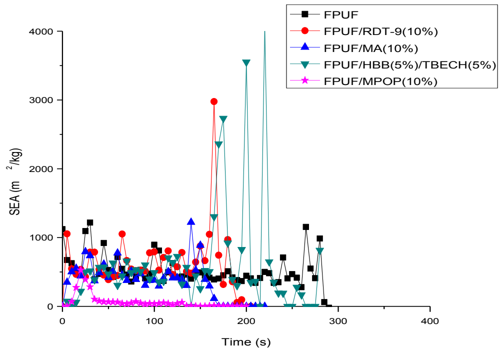


**Fig. 5.** Specific Extinction Area curve of different of FPUF adding different flame retardants.

termination point is taken as the basis of the smoke toxicity levels of the materials. The smoke concentrations and smoke toxicities show opposite trends. The results are shown in Figure 6. The blank specimen as well as the FPUFs with the flame retardant additives MA, RDT-9 and MPOP up to 10% wt all reached class ZA3, in which reaction phenomena that included tears and closed eyes were observed. The smoke toxicities of the FPUFs with HBB and TBECH additives varied gradually. When the concentration of these flame retardants reached 4%, the smoke toxicities reached class WX, in which the mice were comatose.

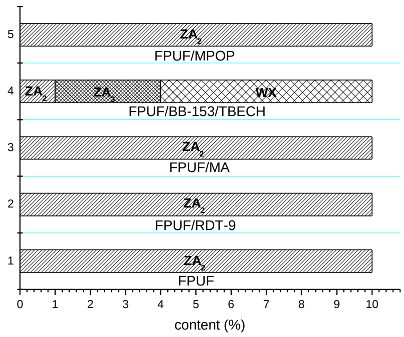


**Fig. 6.** Smoke concentrations and smoke toxicities.

## CONCLUSIONS

FPUFs were prepared by a one step method using different flame retardant additives. The combustion performances of the FPUFs were then tested by evaluating their oxygen indices (OI) and smoke toxicities and by the use of a cone calorimeter (Cone). The results showed that the flame performances of FPUFs prepared with 10% wt brominated flame retardants and 10% wt MPOP were superior. However, the smoke toxicity of the former showed a greater risk, and the smoke toxicity reached the WX level when brominated flame retardants of more than 4% wt were added. In the coordination of N and P, the FPUF with the MPOP additive showed ideal flame retardant properties. It is worth noting that when the content of MPOP exceeds 10%, the physical performance of the FPUF decreases rapidly due to increased brittleness and hardness.

Halogenated flame retardants have high smoke risk, and therefore, they have been gradually phased out. The flame retardant capabilities of non-halogen and coordinative flame retardants are promising, and thus, these additives have become the future direction in the development of flame retardant products. For the preparation of FPUF composite materials with excellent comprehensive performances, the development of coordinative flame retardants and functional research on organic and inorganic additive types, intumescent flame retardants and reactive halogen-free flame retardants will represent the general trend.

## REFERENCES


1. N. Usta, *J. Appl. Polymer Sci.*, **124,** 3372 (2012).
2. M. Ravey, E.M. Pearce, *J. Appl. Polymer Sci.*, **63**, 47 (1997).
3. Zhang Xiaoguang, Wang Lieping, *Chem. Ind. Eng. Progr.*, **31**, 1521 (2012).
4. Liu Yijun, The Synthesis and Application of Polyurethane. Beijing: Chemical Industry Press, 2012, pp.122-138.
5. Shu Zhongjun, Xu Xiaonan, Li Xiang. Fire Performance Evaluation of Polymer Materials, Beijing: Chemical Industry Press, 2007, pp. 61-62.
6. Tian Shi, She-Jun Chen., *Chemosphere*, **74**, 910 (2009).


# ЕФЕКТ НА ДОБАВКИ, ЗАБАВЯЩИ ОГЪНЯ ВЪРХУ ГОРЕНЕТО НА ГЪВКАВА ПОЛИУРЕТАНОВА ПЯНА


Чен Йингджи[1*], Лю Жипенг[1], Дай Пенганг[1], Лю Лан[2]

[1] *Институт за изпитания и наблюдение качеството на продукти Гуангдонг, Гуангджу, Китай*

[2]*Колеж по химия и инженерна химия „Сун Ят-сен“, Гуангджу, Китай*


Постъпила на 12 април, 2014 г.


(Резюме)

В настоящата работа се изследва горенето на гъвкава полиуретанова пяна (FPUFs), приготвена в едностадиен метод с различни добавки, забавящи огъня. Режимът на горене на FPUF е изпитан оценявайки кислородни индекс (OI) и токсичността на дима чрез конична калориметрия (Cone). Резултатите показват, че полиуретаните, приготвени с 10% бромирани забавители и 10% триазин триамин фосфат (MPOP) имат подобрени качества. Максималните скорости на топло-поглъщане са съответно 284.0 Kw/m$^2$ и 270.8 Kw/m$^2$, при излъчване от 30 kW/m$^2$ на проби с дебелина 50 mm. Обаче токсичността на дима показва по-големи вреди, а когато FPUF съдържа повече от 4% бромиран забавител, токсичността достига WX-ниво.