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The Effects of Oxygen Contents and Heating Rates on Characteristics of Pyrolysis Prior to Smoldering of Flexible Polyurethane Foam

HU Shi-qiang, YOU Fei *

College of Urban Construction and Safety Engineering, Nanjing University of Technology, Nanjing, Jiangsu, China, 210009

Abstract

The Simultaneous Differential Scanning Calorimeter-thermogravimetric analyses (DSC-TGA) apparatus was used to investigate the influences of different oxygen contents and heating rates on properties of pyrolysis phase (from room temperature to 800°C) prior to smoldering establishment of polyurethane foam. Results show that reduction of both oxygen content and heating rate show inhibition effects on the pyrolysis of polyurethane foam, i.e., both cases can reduce the propagation rate of smoldering and the possibilities of its transition to flaming. The reduction of the heating rates mainly prolongs pyrolysis cycle, and thus the concentrations of produced volatiles and heat release rates are both descended. However, the influence of oxygen contents on polyurethane pyrolysis is relatively complicated. When oxygen content is less than 10% (volume ratio in mixed nitrogen-oxygen atmosphere), it is the decomposition temperature of polyurethane foam that is enhanced; when the oxygen content is between 10% and 50%, it is the pyrolysis rates, heat release rates and the amount of heat release that are reduced. In addition, the reductions of oxygen contents and heating rates inhibit the decomposition process of polyol that are the main material and energy source to maintain the smoldering propagation or its transition to flaming of polyurethane foam.

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Keywords: flexible polyurethane foam: pyrolysis property; smoldering; oxygen content: heating rate.

1. Introduction

Flexible polyurethane (PU) foam is one kind of polymer materials that have an open cell structure. It has wide application in household and industrial fields for its excellent performance. The scale of PU industry in China will reach 9-10 million tons by 2015, ranking first in the world, which includes 1.8-2 million tons of flexible PU foam, according to China Industry Association of polyurethane. Flexible polyurethane foam is prone to smoldering, thus more amount of toxic and combustible gases are released than flaming, which causees more risk in application. According to a survey, 1/3 of residential fires were originated from soft furniture [1]. Therefore,to understand and control of smoldering well, it is significant to research the characteristics of pyrolysis prior to smoldering of flexible polyurethane foam fathery.

Considerable experimental and theoretical work have been conducted on thermal stability and flame retardancy of polyurethanes [2], others mainly concentrated in the decomposition mechanism or the pyrolysis kinetics of polyurethanes^[3-8]. Few researches were conducted to study the effects of experimental conditions on the pyrolysis characteristics of flexible polyurethane foam. Lucas et al. [9-11] measured pyrolysis products and heat release rates of polyurethane under different heating rates and temperatures. Daniela and Xue et al. [12,13] studied the pyrolysis process of polyurethane under different atmosphere, but only limited to nitrogen and air atmosphere. Oxygen concentration distribution is diverse in different reaction zones in actual smoldering, so it is significant to study the effects of oxygen contents on the pyrolysis of flexible polyurethane foam. From the research we can learn more about smoldering and its transition to flaming of flexible

* Corresponding author. Tel.: +86-25-83239949; fax: +86-25-83239949.

E-mail address: yfei@ustc.edu.cn

Polyurethane foam. Furthermore, most materials used in previous studies are synthesized in laboratory in order to avoid the additive influence on the pyrolysis of polyurethane, whereas commercial polyurethanes were used rarely. Commercial polyurethanes are chemically complex and contain thermally and hydrolytically labile groups such as urea, biuret, allophanate, ether and ester moieties, as well as various additives^[14], so the conclusions based on the laboratory-synthesized materials do not reflect actual smoldering characteristics.

2. Materials and methods

2.1. Material and instrument

Material and instrument	Type	Source
flexible polyurethane foam	Commercial	the company of Sinomax Polyurethanes (Shanghai) Co., Ltd
SDT (simultaneous DSC-TGA)	Q600	TA Instrument (USA)

2.2. Methods

2.2.1 Experiments under different oxygen contents

Experimental material, flexible polyurethane foam, was divided into 7-9mg, and was squeezed into a Sample Crucible. The Sample Crucible filled with material and the empty Reference Crucible was placed on two weighing rods of the experimental instrument respectively, and then began to heat. The tested foams were heated to 800°C in seven pyrolysis atmospheres with different volume ratios of oxygen-nitrogen (0:10, 1:9, 2:8, 3:7, 4:6, 5:5 and air) but the same gas velocity, 100ml/min ,and heating rate, 10K/min. The information of weight loss and heat flux of the pyrolysis process were recorded by the experimental instrument SDT Q600.

2.2.2 Experiments under different heating rates

The experiment procedure of this part is similar to the above except the different experimental conditions. In this part, air was selected as the pyrolysis atmosphere. The tested foam was heated to 800°C at three heating rates(10, 20, 50 K / min) respectively with the same velocity (100ml/min).

3. Results and analysis

3.1. The effects of oxygen contents

There are seven groups of experiment in first part, and four set of the date (oxygen contents are 0, 10, 30, 50%) were selected for analysis. Results are shown in Fig. 1 to Fig. 3, which represent its TG, DTG and DSC data of the flexible PU foam decomposition. The temperatures values at different pyrolysis phase of the tested foam under different oxygen contents are summarized in Table 1.

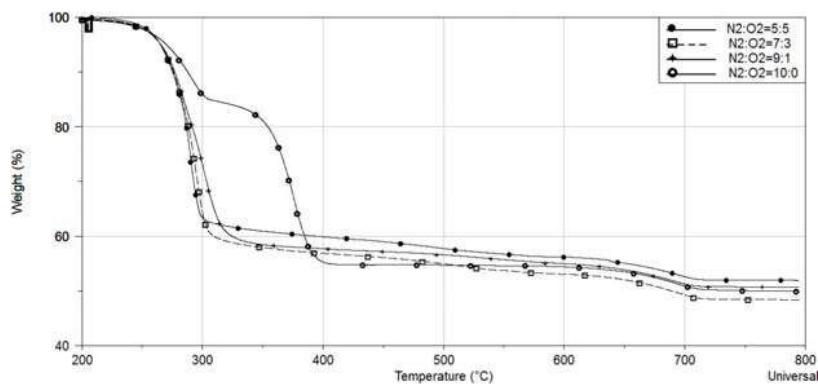


Fig. 1 TG curves of the tested foam under different atmospheres (heating rate 10K/min)

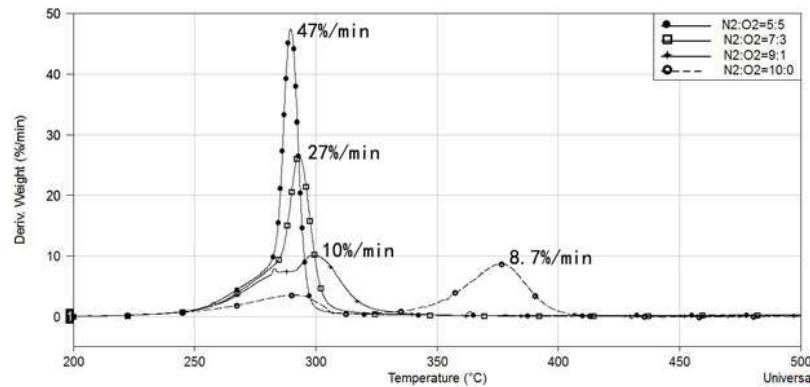


Fig. 2 DTG curves of the tested foam under different atmospheres(heating rate 10K/min)

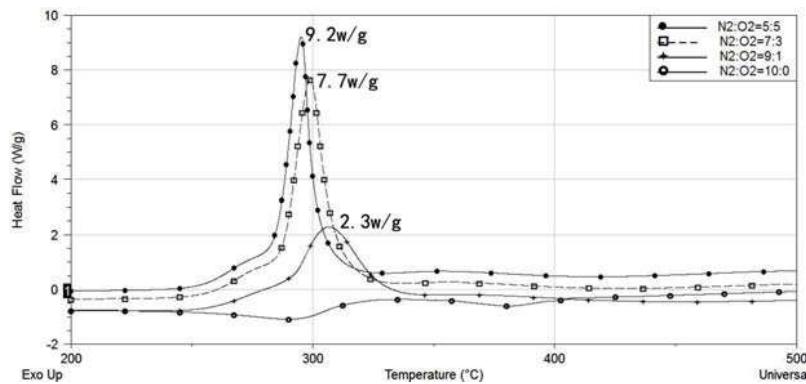


Fig. 3 DSC curves of the tested foam under different atmospheres(heating rate 10K/min)

Table 1 The temperatures at different pyrolysis phase of the tested foam under different oxygen contents

N ₂ :O ₂	Initial temperatures of main pyrolysis stage(°C)	Final temperatures of main pyrolysis stage(°C)	Temperatures at maximum weight loss rate(°C)
5:5	237	312	290
7:3	238	324	293
9:1	236	338	300
10:0	238	404	377

Fig. 1 to Fig. 3 shows the temperature of main weight loss and pyrolysis stage is between 240°C and 400°C. To guarantee accurate values, only if weight loss rate (ordinate of Fig. 2) is above 0.5%/min, the stage is defined as main pyrolysis. Because if weight loss rate is below 0.5%/min, it indicates that pyrolysis process is extremely slow and even has completed. Therefore, the temperature of main pyrolysis stage is between 240°C and 340°C under oxygen-containing atmosphere, while it is between 240°C and 405°C under nitrogen atmosphere (Table 1). Fig. 3 shows that the main pyrolysis stage is correspond to main exothermic stage. Besides, the main pyrolysis stage provides major material and energy for its smoldering, so it is the key research stage in this paper.

The main pyrolysis stage of PU consists of complex physical and chemical reactions, so it is difficult to depict the detailed mechanism of pyrolysis process. It is accepted that PU breaks down in the C-O bond generating isocyanate and polyol firstly, then the decomposition or carbonization of polyol begin with the further increasing of the temperature^[15]. However, large numbers of experiments confirmed that in open vessels it is volatilization rather than decomposition^[3,16] to make isocyanate loss weight associated with brown-yellow smoke. This conclusion also is confirmed by Fig. 4, which shows the tested foam turns into brown-yellow (caused by the volatilization of isocyanate) at 250°C. It's beginning decomposition temperature of tested foam. Fig. 1 and Fig. 2 clearly show that the degradation of the flexible PU foam occurs in two steps. The first weight loss step can be considered as the volatilization of isocyanate, and the second weight

loss step is associated with the decomposition of polyol^[6,10]. In addition, toxic and harmful gases mostly are generated in this main pyrolysis stage, such as HCN, CO₂, CO, NO_x, isocyanate, amines, alkenes, alkanes, and other toxic and flammable substances.

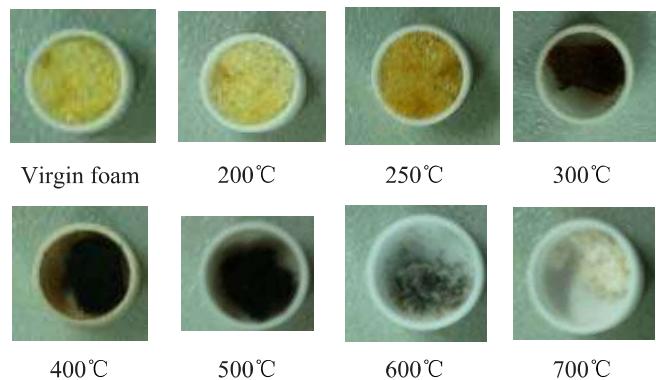


Fig. 4 The surface morphology of the tested foam decomposed to different temperatures under air atmosphere (heating rate 10K/min)

The effects of oxygen content on the pyrolysis characteristics of flexible PU foam are shown in Fig. 1 to Fig. 3. The decreasing of oxygen content inhibits the pyrolysis of flexible PU foam, because both of the weight loss rates and heat release rates reduced with its decreasing, whereas the pyrolysis temperatures increased and the pyrolysis curves shifted to high temperature. However, the initial temperatures of main pyrolysis stage shown in table 1 are nearly 237°C, which indicates that the oxygen content has little effect on decomposition reaction from flexible PU foam to isocyanate and polyol.

Fig. 2 clearly shows that when oxygen content ranges from 10% to 50%, the DTG curves have only one peak; when oxygen contents reduced from 10% to zero, the DTG curve turned into two peaks gradually. The results also confirmed by other experimental^[10, 13, 17-18]. The two steps follow the volatilization of isocyanate and the decomposition of polyol under nitrogen atmosphere respectively based on the analysis before^[10]. Therefore, the reduction of oxygen content mainly suppressed the decomposition of polyol actually.

The weight loss rate of the tested foam under nitrogen atmosphere presented on the DTG curve is nearly zero between 310°C and 330°C (Fig. 2), which indicated the ending of flexible PU foam decomposition into isocyanate and polyol, but the decomposition of polyol has not yet started. Therefore, the initial decomposition temperature of the polyol is about 330°C under nitrogen atmosphere. Thus, we can calculated from Fig. 1 that the weight loss of the two steps are 14.5% and 29.8%, which corresponds to the volatilization of isocyanate and the decomposition of polyol respectively. From Fig. 2 and Fig. 3, both weight loss rates and heat release rates increase greatly at about 280°C under the three types of oxygen-containing atmosphere. It indicates the decomposition of polyol started at about 280°C.

Fig. 2 and Fig. 3 show that the weight loss rates and heat release rates all decreases with the reducing of oxygen content. When oxygen content decreases from 50% to 10%, the maximum rates of weight loss reduces from 47%/min to 8.7%/min and the maximum rates of heat release reduces from 9.2w/g to 2.3 w/g. The changes are caused by the suppression on the decomposition of polyol by the decreasing of oxygen content based on the analysis before. Therefore, the polyol is the main material and energy source to maintain the smoldering propagation and its transition to flaming of flexible polyurethane foam.

Fig. 2 and Fig. 3 present some special features of pyrolysis process. When oxygen content decreases from 50% to 10%, the maximum rates of weight loss and heat release reduce greatly, whereas the temperatures at maximum weight loss rate and final temperatures of main pyrolysis stage only increase 10°C and 26°C respectively. When oxygen content decreases from 10% to zero, change in weight loss rates is relatively small, whereas the temperatures at maximum weight loss rate and final temperatures of main pyrolysis stage are increases apparently by 77°C and 66°C respectively. So we can concluded that the influence of reducing oxygen contents on the pyrolysis of flexible PU foam can be separated into two cases. When the oxygen content is between 10% and 50%, the reduction of oxygen content mainly reduces the pyrolysis rate and heat release rate; when the oxygen content is less than 10%, the reduction of oxygen content mainly enhances the decomposition temperature of flexible PU foam.

3.2. The effects of heating rates

Fig. 1 to Fig. 3 present the TG, DTG and DSC data obtained from the decomposition of flexible PU foam at three heating rates (10, 20, 50K/min) under air atmosphere.

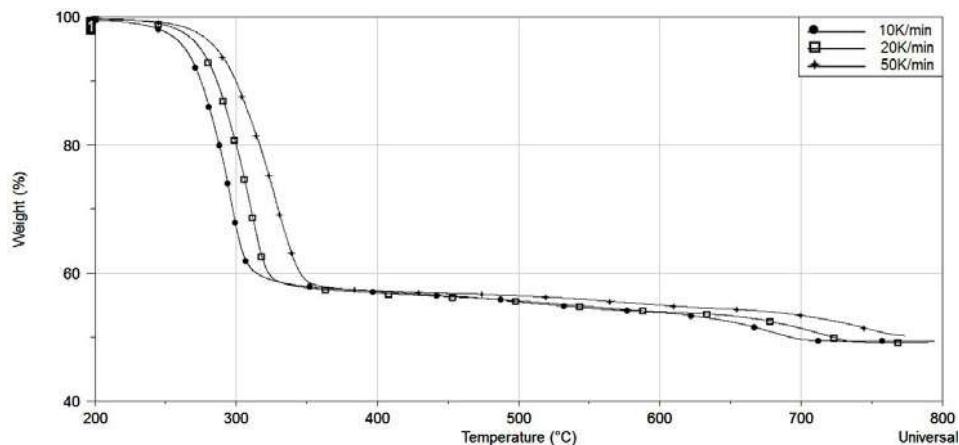


Fig. 5 TG curves of the tested foam at different heating rates under air atmosphere

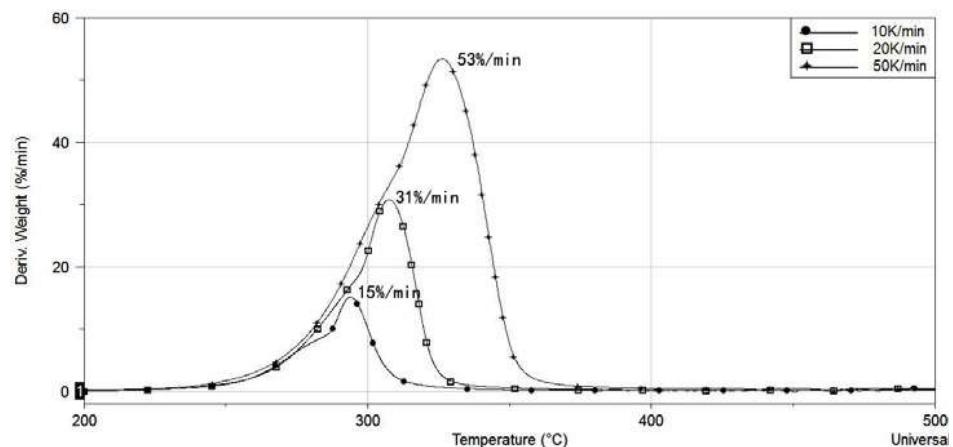


Fig. 6 DTG curves of the tested foam at different heating rates under air atmosphere

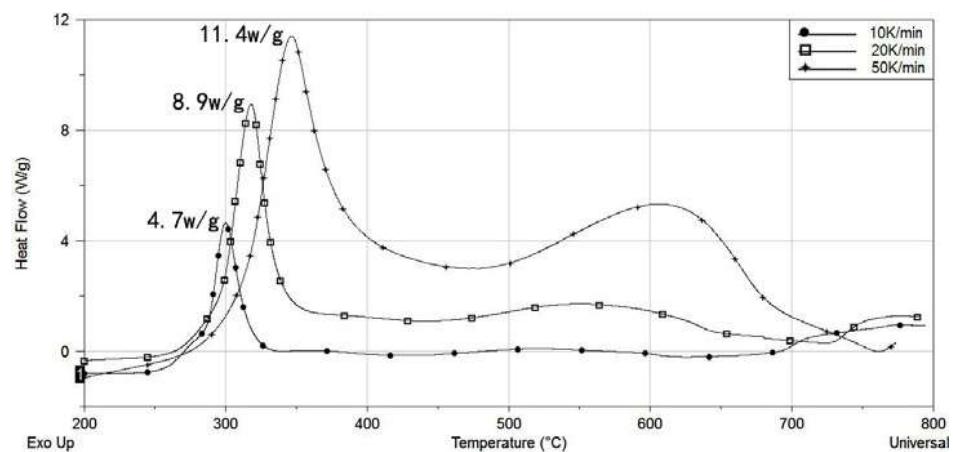


Fig. 7 DSC curves of the tested foam at different heating rates under air atmosphere

Table 2 The results of the selected parameters obtained from figure 6

Heating rates (K/min)	Initial temperatures and times of main pyrolysis stage(°C)		Final temperatures and times of main pyrolysis stage(°C)		Temperature and times at maximum weight loss rates(°C)	
	Temperatures(°C)	Times (min)	temperatures(°C)	Times (min)	temperatures(°C)	Times (min)
10	236	20.2	331	29.6	294	25.7
20	234	10.2	354	16.2	308	13.7
50	233	4.4	396	7.6	326	6.2

Fig. 5 and Fig. 6 show the change in heating rates have no effect on the shape of pyrolysis curves, i.e. heating rate has no effect on the pyrolysis mechanism of flexible PU foam. Table 2 presents the initial temperatures of the main pyrolysis stage keep at about 235°C despite the heating rate is changed, which is similar to the initial temperature of main pyrolysis stage at 237°C under different oxygen contents. Therefore, the initial temperatures of main pyrolysis stage have no correlation with heating rate and oxygen content. However, the temperatures at maximum weight loss rate and final temperatures of main pyrolysis stage increases greatly by 32°C and 65°C respectively (table 2), and the DTG curves tends to higher temperature (Fig. 6).

The pyrolysis temperature increases. It doesn't mean that the enhancement of increasing heating rate inhibits the decomposition of flexible PU foam but the heating process from medium - container – sample works. There is a temperature difference between the furnace and the tested foam, and a temperature gradient inside the specimen. The improvement of heating rates exacerbates the non-balance process, i.e., temperature difference increases with the heating rates increasing. Therefore, as heating rate increases, pyrolysis temperature increases, and the pyrolysis of flexible PU foam is delayed.

Fig. 6 and Fig. 7 show that when heating rate increases from 10 K/min to 50 K/min, the maximum weight loss rate increases from 15%/min to 53%/min, and the maximum heat release rate increases from 4.7w/g to 11.4w/g. The increasing of weight loss rate results a faster smoldering propagation, higher concentration of pyrolytic gas, while the increasing of heat release rate causes higher smoldering temperature. Furthermore, when heating rates increases from 10K/min to 50K/min, the pyrolysis cycle (final times of main pyrolysis stage subtract initial times of main pyrolysis stage) of flexible PU foam reduces from 9.4min to 3.2min, i.e. it accelerates the smoldering propagation. Therefore, the increase of heating rates enhances the pyrolysis rate, heat releases rate and shortens the pyrolysis cycle, and thus promotes the smoldering propagation and its transition to flaming.

4. Conclusions

(1) Flexible PU foam decomposed into isocyanate and polyol firstly, and then attained the decomposition of polyol at higher temperature. Oxygen content has no effects on the first decomposition reaction. But polyol decomposed at about 280°C under oxygen-containing atmosphere, while at 330°C under nitrogen atmosphere.

(2) The decreasing of oxygen content inhibits the pyrolysis of flexible PU foam, due to the suppressed decomposition of the polyol. The polyol is the main substance that affects the smoldering characteristics of flexible PU foam, and it is also the main material and energy source to maintain the smoldering propagation and its transition to flaming.

(3) The influence of reducing oxygen contents on the pyrolysis of flexible PU foam can be separated into two cases. When oxygen content is between 10% and 50%, the reduction of oxygen content mainly reduces the pyrolysis rates and the heat release rates; When the oxygen contents are less than 10%, the reduction of oxygen content mainly enhances the decomposition temperature of flexible PU foam.

(4) The increase of heating rates mainly accelerates the pyrolysis rate, heat release rate and shortens pyrolysis cycle, thus the smoldering velocity, smoldering emissions and temperature are increased. All of the factors promote the smoldering propagation, and its transition to flaming of flexible PU foam.

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References

- [1] CR Wong. contribution of upholstered furniture to residential fire fatalities in New Zealand[R]. New Zealand, 2001.
- [2] D. K. Chattopadhyay, Dean C. Webster. Thermal stability and flame retardancy of polyurethanes[J]. Progress in Polymer Science, 2009, 34: 1068-1133.
- [3] W. D. Woolley. Nitrogen-containing products from the thermal decomposition of flexible polyurethane foams[J]. British Polymer Journal, 1972, 4(1): 27-43.
- [4] R. Bilbao, J. F. Mastral, J. Ceamanos et al. Kinetics of the thermal decomposition of polyurethane foams in nitrogen and air atmospheres[J]. Journal of Analytical and Applied Pyrolysis, 1996, 37(1): 69-82.
- [5] Sergei V. Levchik, Edward D. Weil. Thermal decomposition, combustion and fire-retardancy of polyurethanes - A review of the recent literature[J]. Polymer International, 2004, 53(11): 1585-1610.
- [6] Ante Agić, Emi Govorčin Bajšić. Strategy for kinetic parameter estimation—Thermal degradation of polyurethane elastomers[J]. Journal of Applied Polymer Science, 2007, 103(2): 764-772.
- [7] A. B. Dodda, C. Lautenbergerb, A. C. Fernandez-Pellob. Numerical examination of two-dimensional smolder structure in polyurethane foam[J]. Proceedings of the Combustion Institute, 2009, 32(2): 2497-2504.
- [8] T. Rogaume, LB Valencia, E. Guillaume. Development of the Thermal Decomposition Mechanism of Polyether Polyurethane Foam Using Both Condensed and Gas-Phase Release Data[J]. Thermal stability and flame retardancy of polyurethanes, 2011, 138(7): 627-644.
- [9] L. Bustamante Valencia, T. Rogaume, E. Guillaume. Analysis of principal gas products during combustion of polyether polyurethane foam at different irradiance levels[J]. Fire Safety Journal, 2009, 44(7): 933-940.
- [10] RH Krämer, M. Zammarano, GT Linteris. Heat release and structural collapse of flexible polyurethane foam [J]. Polymer Degradation and Stability, 2010, 95(6): 1115-1122.
- [11] Yan hong Zhang, Zheng bin Xia, Hong Huang et al. Thermal degradation of polyurethane based on IPDI[J]. Journal of Analytical and Applied Pyrolysis, 2009, 84(1): 89-94.
- [12] Daniela Włodarczak. Studies of Temperature and Atmosphere Composition Influence on Thermal DegradationProducts of PolyurethaneFoam[J]. Journal of Applied Polymer Science, 1988, 36(2): 377-386.
- [13] Xue Lin, Yang Yun, Xie Qiyuan. experimental study on degradation properties of typical polyurethane foam under different gas atmospheres and different heating rates[J]. Journal of Applied Fire Science, 2007, 17(2): 167-175.
- [14] Jozef Rychlýa, Agnes Lattuati-Derieuxb, Bertrand Lavédrinebet al. Assessing the progress of degradation in polyurethanes by chemiluminescence and thermal analysis. II. Flexible polyether- and polyester-type polyurethane foams [J]. Polymer Degradation and Stability, 2011, 96(4): 462-469.
- [15] Stephen Da-Yen Tse. An Experimental Investigation of Two-Dimensional Smoldering and the Transition to Flaming in Flexible Polyurethane Foam[D]. California: UNIVERSITY of CALIFORNIA, BERKELEY, 1996.
- [16] M. Ravey, Eli M. Pearce. Flexible polyurethane foam. I. Thermal decomposition of a polyether-based, water-blown commercial type of flexible polyurethane foam[J]. Journal of Applied Polymer Science, 1997, 63(1): 47-74.
- [17] Yaping Gao, Xiao Wang. Effect of N-P cooperative flame retardant on pyrolysis characteristics of soft PU foam(in Chinese)[J]. Engineering Plastic Application, 2011, 39(4): 60-63.
- [18] Anna Wolska, Marcin Goździkiewicz, Joanna Ryszkowska. Thermal and mechanical behaviour of flexible polyurethane foams modified with graphite and phosphorous fillers[J]. Journal of Materials Science , 2012, 47(15): 5627-5634.