TG-FTIR characterization of flame retardant polyurethane foams materials

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Abstract. Dimethyl methylphosphonate (DMMP) and trichloroethyl phosphate (TCEP) have been used to enhance the flame retardancy of polyurethane foams materials (PUF). Flame retardancy and thermal degradation of PUF samples have been investigated by the LOI tests and thermal analysis. The results indicate that the excellent flame retardancy can be achieved due to the presence of the flame retardant system containing DMMP and TCEP. TG-FTIR reveals that the addition of DMMP/TCEP can not only improve the thermal stability of PUF samples but can also affect the gaseous phase at high temperature.

1. Introduction
Polyurethane foam (PUF) as an organic insulation material is of great interest to many consumers due to its excellent properties including good mechanical properties, low cost and effective thermal insulation [1-3]. However, like some other organic materials, the flammability of PUF limits its use in many areas. During the period of 2000-2010, many fire originated from PUF insulation materials has been reported in China. And the investigation from these accidents suggests that the hazard during combustion of the PUF can be caused by not only the high burning heat but also the release of the volatile products formed during its thermal degradation at high temperature, which could induce asphyxia, coma or death of people.

In our research, dimethyl methylphosphonate (DMMP) and trichloroethyl phosphate (TCEP) have been used as the flame retardants containing phosphorus and halogen to improve the flame retardancy of the PUF samples. Many previous literatures have reported that DMMP and TCEP are the traditional flame retardants to enhance the thermal stability of materials at high temperature range. However, the influence of these flame retardants on the pyrolysis products in the gaseous phase during thermal degradation of PUF has been rarely mentioned. In this study, flame retardancy and thermal stability of PUF containing DMMP and TCEP have been investigated. TG-FTIR analysis has been used to characterize the change of the pyrolysis products in the gaseous phase during heating of the samples here. The aim of this work is to investigate the thermal degradation characteristics of the PUF samples and the influence of DMMP and TCEP on the gaseous phase at high temperature range.

2. Experimental

2.1. Materials
Polyether polyl (Model: 4110, 635) and polyaryl polymethylene isocyanate (PAPI) (Model: GR-4110G) were purchased from Shanghai Gaoqiao Petro Co, China. Cyclohexylamine used as the
catalyst and dichlorofluoroethane (HCFC-141b) used as the foaming agent were obtained from Changzheng Chemical Reagent Company, China. Dimethyl methylphosphonate (DMMP) and trichloroethyl phosphate (TCEP) were supplied from Jinan Enter Chemical Co., Ltd.

2.2 Preparation
Polyurethane foam samples were prepared by the cast molding method. Polyether polyol was mixed with cyclohexylamine, HCFC-141b, DMMP, TCEP, water together, and then stirred with an electric stirrer at the agitation speed of 1500 r/min until the solution was uniform. Then PAPI was added into the solution and stirred for 90s with the speed of 500 r/min. Thereafter, the solution was cast into a mold and then heated at 70°C for 48hr. Finally, polyurethane foam samples were taken out from the mold for using.

2.3 Measurements

2.3.1 LOI. The limiting oxygen index (LOI) tests were carried out on a JF-3 type instrument (Jiangning, China), according to GB/T 2406-1993.

2.3.2 TG-FTIR. Thermogravimetric analysis-infrared spectrometry (TG-FTIR) of the PUF samples was performed using DT-50 instrument that was interfaced to IRAffinity-1 FTIR spectrometer. About 5 mg of the PUF sample was put in an alumina crucible and heated from 25 to 800°C in nitrogen atmosphere with the heating rate of 10°C/min.

3. Results and discussion

3.1 Flame retardancy
LOI values of polyurethane samples are presented in table 1. It indicates that LOI value of the PUF samples increase with flame retardant concentration, the % P value and the % Cl value. The higher the % P value and the % Cl value, the higher the LOI value. LOI values of all the flame retardant PUF samples are higher than that of the neat sample (23.0%). PUF/DMMP-TCEP (30%) has the highest LOI value of 30.6%, which is much higher than that of PUF sample without flame retardant containing phosphorus and chloride. It is suggested that the improved flame retardancy of PUF samples is attributed to the presence of DMMP and TCEP. And in the limiting oxygen index test, it can be observed that the intumescent residual char layer can be formed as a barrier between flame and the flame retardant PUF samples to inhibit the transmission of heat, energy and O2 during combustion [4, 5]. The results reveal that the flame retardant system containing DMMP and TCEP could improve the flammability of polyurethane foam materials.

| Samples | DMMP Concentration (w/w %) | TCEP Concentration (w/w %) | P %  | Cl %  | LOI (%) |
|---------|-----------------------------|-----------------------------|------|-------|---------|
| 1       | 0                           | 0                           | 0    | 0     | 23.0    |
| 2       | 14                          | 6                           | 4.2% | 2.2%  | 27.4    |
| 3       | 21                          | 9                           | 6.2% | 3.3%  | 30.6    |

3.2 Thermal analysis (TGA)
Thermogravimetric (TG) and derivative thermogravimetric (DTG) were used to investigate the thermal stability of the PUF samples in detail. TG curves of the samples are shown in figure 1. It can be seen that starting decomposition temperature of the flame retardant samples are 223°C (20% DMMP/TCEP) and 190°C (30% DMMP/TCEP), respectively, which are lower than that of the PUF.
sample. The higher % P value, the lower the starting decomposition temperature. This can be attributed to the earlier decomposition of P-O-C from DMMP and TCEP during the thermal degradation of the flame retardant PUF sample due to its lower bond energy, which could form some compounds containing phosphate to catalyze the formation of the residual layer at high temperature [6, 7]. Residue of the flame retardant PUF sample containing 20% DMMP/TCEP (Sample 2) at 800°C is higher than that of the neat PUF sample. However, sample 3 containing 30% DMMP/TCEP has the lowest residual amount of 14.0% at 800°C compared with the neat PUF sample (14.1%) and the PUF sample containing 20% flame retardants (16.7%). DTG curves from figure 2 show that the Sample 2 has three maximal weight loss peaks while the PUF sample has two maximal weight loss peaks. Compared the neat sample, the small new peak can be observed at the relative low temperature range for Sample 2, which could be explained by the thermal degradation of flame retardant containing phosphorus to catalyze the release of water and some volatile compounds during the decomposition of the sample. Meanwhile, Sample 3 containing 30% DMMP/TCEP has one more weight loss peak at the temperature range of 375-421°C compared with Sample 2. This could be due to the gaseous flame retardant action of the higher content TCEP containing chloride at high temperature range. These results suggest that flame retardant system containing DMMP and TCEP could change the thermal degradation process of the PUF sample.

![Figure 1. TG Curves of PUF samples](image1.png)

![Figure 2. DTG curves of PUF samples](image2.png)
3.3 TG-FTIR

The gaseous products produced by pyrolysing various samples of the neat PUF and flame retardant PUF samples in nitrogen at different temperature (50-800°C) have been investigated by TG-FTIR. Figure 3, 4 and 5 shows the 3D and 2D TG-FTIR spectra of neat PUF, PUF with 20% DMMP/TCEP and PUF with 30% DMMP/TCEP. As shown in figure 3, absorption peaks at 1114cm⁻¹, 1257cm⁻¹, 1220cm⁻¹-1320cm⁻¹, 3318cm⁻¹, 1622cm⁻¹ and 2275cm⁻¹ can be assigned to C-O-C, C-O from ester, C-N from amine group, N-H, -C=C and -NCO from neat PUF sample, respectively [8~10]. Sample 2 with 20% DMMP/TCEP has less and lower absorption peaks at high temperature range compared to neat PUF sample (figure 4), which indicates the lower evolution of the gaseous products during its thermal degradation process. This can be explained by the formation of the thick char layer covering the underlying PUF matrix due to the condensed flame retardant action of flame retardant containing phosphorus, which prevents the further thermal degradation of the sample in high temperature [11]. However, the more and higher absorption peak of Sample 3 with 30% DMMP/TCEP can be observed at high temperature range in figure 5, indicating the large release of the pyrolysis products to the gaseous phase. Combined with the high LOI value of Sample 3, this can be attributed to the gaseous flame retardant action of the flame retardant system containing DMMP and TCEP due to the higher content of chloride compared to Sample 2, which is in accordance with the results from thermal analysis of the PUF samples in Section 3.2.

![Figure 3](image1.png)

**Figure 3.** 3D and 2D TG-FTIR spectra of PUF without DMMP and TCEP

![Figure 4](image2.png)

**Figure 4.** 3D and 2D TG-FTIR spectra of PUF/DMMP-TCEP (20)
FTIR spectra of neat PUF sample obtained at the maximum evolution rates (340 and 479 °C) during heating are presented in figure 6, which can be used to get more information about the pyrolysis product in the gaseous phase. The characterized peaks of -NCO (2275 cm⁻¹), CO₂ (2352 cm⁻¹), H₂O (3579 cm⁻¹) and -NH from -NHC=O (1530 cm⁻¹) can be observed in spectrum (a) at 340 °C, indicating that the depolymerisation of polyurethane and the break of its main chains [12]. In spectrum (b) at 479 °C, the peaks at 1530 cm⁻¹ and 2275 cm⁻¹ have almost disappeared while some other peaks at 1513 cm⁻¹, 2905 cm⁻¹, 1465 cm⁻¹, 1626 cm⁻¹ and 935 cm⁻¹ can be observed, which could be assigned to phenyl, -CH₃, -CH₂, and C=C and -CH₂ from alkene[13]. It suggests that thermal degradation of PUF materials can be described as two steps: the depolymerization of the main chains and the further pyrolysis of polyol and isocyanate [14].

**Figure 5.** 3D and 2D TG-FTIR spectra of PUF/DMMP-TCEP (30)

**Figure 6.** FTIR spectra of PUF at the maximal weight loss rates: (a) 340 °C; (b) 579 °C
FTIR spectra of Sample 2 at the maximum evolution rates (136, 335 and 474 °C) during heating are presented in figure 7. In spectrum (a) at 136 °C, the absorption peaks of 1099 cm⁻¹, 923 cm⁻¹, 764 cm⁻¹ and 678 cm⁻¹ can be observed, which are assigned to C-O, P-C, P-O and C-Cl [15]. Absorption peak of HCl has appeared at 2860 cm⁻¹. These results confirm the decomposition of TCEP and DMMP at the initial decomposition stage, which is also supported by the result from TG and DTG presented in figure 2 and 3. Absorption peak of HCl at 2860 cm⁻¹ has disappeared at 335 °C. It may be due to the gaseous flame retardant action of TCEP containing chloride to capture the radical during combustion. Meanwhile, the peak of P=O at 1320 cm⁻¹ can be observed in spectrum (b) [16]. The peak of P=O has disappeared at 474 °C, indicating the flame retardant action of DMMP containing phosphorus in gaseous phase at high temperature range. However, the lower and less absorption peaks in spectrum (c) confirms that flame retardant activity of Sample 2 mainly takes effect in the condensed phase.

4. Conclusions
Dimethyl methylphosphonate (DMMP) and trichloroethyl phosphite (TCEP) have been used as the flame retardants containing phosphorus and chloride to improve flame retardancy and thermal stability of the polyurethane foam material by the cast molding method. The LOI tests show that the LOI value of the PUF sample increases with the DMMP and TCEP concentration Thermal stability of the flame retardant sample can be enhanced at high temperature. Meanwhile, based on the information from TG-FTIR analysis, it can be concluded that although the flame retardant system containing DMMP and TCEP could improve the thermal stability of PUF samples by the formation of the intumescent residual char in the condensed phase, which covers the substrate to retard the thermal degradation of material, the release of the gaseous products can be also influenced due to the presence of DMMP and TCEP at high temperature.

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References

[1] Grace T C, Salvador C N and Francisco V 2012 *Frontiers of Architectural Research* 1 348
[2] Hu S J and Li Y B 2014 *Bioresour. Technol.* 161 410
[3] Adel R K, Mustafa K, Kyle M, Mohini S and Oh S K 2015 *Ind. Crop. Prod.* 74 1
[4] Wang D Y, Ge X G, Wang Y Z, Wang C, Qu M H and Zhou Q 2006 *Macromol. Mater. Eng.*, 291 638
[5] Liu W, Chen D Q, Wang Y Z, Wang D Y and Qu M H 2007 *Polym. Degrad. Stab.* 92 1046
[6] Tian G X, Ji Q, Xu D M, Tan L W, Quan F Y and Xia Y Z 2013 *Fiber Polym.* 14 767
[7] Chen D Q, Wang Y Z, Hu X P, Wang D Y, Qu M H and Yang B 2005 *Polym. Degrad. Stab.* 88 349
[8] Liu W, Zhang S, Bourbigot S, Sun J, Yu L H, Feng Q L, Chen X S and Zhu XJ 2012 *Polym. Adv. Technol.* 23 1550
[9] Hu J H and Zhen X F 2011 Bei Jing *Science Press* 286
[10] Wei L L, Wang D Y, Chen H B, Chen L, Wang X L and Wang Y Z 2011 *Polym. Degrad. Stab.* 96 1557
[11] David W H, Gayani K and John M K 2005 *Polym. Degrad. Stab.* 87 555
[12] Chen X L, Huo L L, Jiao C M and Li S X 2013 *J. Anal. Appl. Pyrol.* 100 186
[13] Jiao L L, Xu G D, Wang, Q. S, Xu Q and Sun J H 2012 *Thermochim. Acta* 547 120
[14] Cao Z H, Zhang Y, Song P G, Cai Y Z, Guo Q, Fang Z P and Peng M 2011 *J. Anal. Appl. Pyrol.* 92 339
[15] Liu W, Chen L and Wang Y Z 2012 *Polym. Degrad. Stab.* 97 2487
[16] Gu J W, Zhang G C, Dong S L, Zhang Q Y and Kong J 2007 *Surf. Coat. Technol.* 201 7835