Effect of DMMP on the pyrolysis products of polyurethane foam materials in the gaseous phase

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Abstract. Dimethyl methylphosphonate (DMMP) has been used as a flame retardant containing phosphorus to decrease the flammability of the polyurethane foam material (PUF). Flame retardancy and thermal degradation of PUF samples have been investigated by the LOI tests and thermal analysis. The results show that LOI values of all PUF/DMMP samples are higher than that of the neat PUF sample and the LOI value of the samples increases with both DMMP concentration and the %P value. Thermal analysis indicates that flame retardant PUF shows a dominant condensed flame retardant activity during combustion. Thermogravimetric analysis-infrared spectrometry (TG-FTIR) has been used to study the influence of DMMP on the pyrolysis products in the gaseous phase during the thermal degradation of the PUF sample. Fourier transform infrared spectrometry (FTIR) spectra of the PUF sample at the maximum evolution rates and the generated trends of water and the products containing –NCO have been examined to obtain more information about the pyrolysis product evolutions of the samples at high temperature. These results reveal that although DMMP could improve the thermal stability of PUF samples through the formation of the residual char layer between fire and the decomposed materials, the influence of DMMP on the gaseous phase can be also observed during the thermal degradation process of materials.

1. Introduction

Recently, insulation materials have been widely used in construction to meet the energy-saving and emission-reduction requirements from the national building code in many countries. Polyurethane foam 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. In November 2010, the big fire occurred at residential high-rise in Shanghai Jingan district was caused by the ignition of PUF used in the insulation external wall, which made 58 people killed and more than 70 people injured. Another fire in Jilin leaded to the direct economic loss of 5 million and the burned area of 7900 m², which resulted from the combustion of the PUF insulation material used in the roof. Meanwhile, 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.
According to the previous literature, DMMP as the flame retardant containing phosphorus could exhibit a good condensed phase flame retardant during combustion. Many researches have revealed that the flame retardant containing phosphorus could promote the carbonization reaction of the materials and increase its char yield at high temperature, indicating that the condensed phase activity is dominant during burning [4, 5]. However, the influence of DMMP on the gaseous phase during thermal degradation of PUF has been examined in this study. Flame retardancy and thermal stability of PUF containing DMMP have been investigated here. TG-FTIR analysis has been used to characterize the change of the pyrolysis products in the gaseous phase during heating of the samples. The aim of this work is to investigate the thermal degradation characteristics and the pyrolysis product evolutions of the PUF samples at high temperature range.

2. Experimental

2.1. Materials

Polyether polyol (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) was supplied from Jinan Enter Chemical Co., Ltd.

2.2 Preparation of samples

Polyurethane foam samples were prepared by the cast molding method. Polyether polyol was mixed with cyclohexylamine, HCFC-14b, DMMP, water together, and stirred with an electric stirrer at the agitation speed of 1500 r/min until a uniform mixture was formed. Then PAPI was added into the mixture and stirred for 90s with the speed of 500r/min. Thereafter, the mixture 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

The limiting oxygen index (LOI) tests were carried out on a JF-3 type instrument (Jiangning, China), according to GB/T 2406-1993. Thermogravimetric analysis-fourier transform infrared spectrometry (TG-FTIR) of the neat PUF and the flame retardant PUF was performed using DT-50 (Setaram, France) instrument that was interfaced to IRAffinity-1 FTIR spectrometer. About 5 mg of the 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 test has been used to evaluate the flame retardancy of the PUF samples. The LOI value is the minimum concentration of oxygen required to maintain combustion of the material, and is the simplest method to measure flammability of materials [6]. LOI values of the PUF samples are presented in table 1. It indicates that LOI values of all PUF/DMMP samples are higher than that of the neat PUF sample. And LOI value of the PUF samples increases with both DMMP concentration and the %P value. The higher the %P value, the higher the LOI value. PUF/DMMP (30%) has the highest LOI value of 31.0%, which is 8.0% higher than that of the neat sample. It is suggested that the improved flame retardancy of the PUF samples can be attributed to the presence of DMMP. And in the LOI test, the residual char layer (figure 1) can be formed as a barrier between fire and the samples to inhibit the
transmission of heat, energy and O2 during combustion of the flame retardant PUF. This phenomenon reveals that DMMP as the flame retardant containing phosphorus could enhance the flame retardancy of the PUF samples based on the condensed flame retardant mechanism.

**Table 1.** LOI values of PUF samples.

| Samples | DMMP concentration (w/w %) | P% | LOI (%) |
|---------|----------------------------|----|---------|
| 1       | 0                          | 0  | 23.0    |
| 2       | 20                         | 5.0| 27.7    |
| 3       | 30                         | 7.5| 31.0    |

**Figure 1.** Photograph of sample 3 after the LOI tests.

3.2 Thermal analysis

Thermogravimetric (TG) and derivative thermogravimetric (DTG) were used to study the thermal stability of the PUF samples. TG curves of the samples are shown in figure 2. It can be seen that starting decomposition temperature of the PUF/DMMP samples are 252°C (20% DMMP) and 216°C (30% DMMP), respectively, which are lower than that of the neat PUF sample. The higher %P value, the lower the starting decomposition temperature. This may be attributed to the earlier decomposition of DMMP at the initial stage of the whole thermal degradation [7]. And the residual char of the flame retardant samples at 800°C are higher than that of the neat sample. Compared to the other samples, Sample 3 with the DMMP content of 30% has the highest residual char of 16.8%. It indicates the thermal degradation of the flame retardant sample could be inhibited due to the incorporation of DMMP. DTG curves in figure 3 show that Sample 2 and 3 have three maximal weight loss peaks while the neat PUF sample has two maximal weight loss peaks. It is suggested that the presence of DMMP has changed the thermal degradation process of the PUF samples. Meanwhile, it also shows the maximal weight loss rate temperature of flame retardant PUF is lower than that of the neat sample. Among all the samples, sample 3 with the highest %P value of 7.5% has the smallest maximal weight loss rate. These results indicate that the thermal stability of PUF samples can be enhanced with the content of DMMP [8].

**Figure 2.** TG Curves of PU samples.
3.3 TG-FTIR

TG-FTIR analysis has been used to investigate the influence of DMMP on the pyrolysis products in the gaseous phase during the thermal degradation of the PUF sample. Figure 4 and 5 show the 3D and 2D TG-FTIR spectra of the neat PUF sample and the flame retardant PUF sample with the 30% DMMP concentration. As shown in Figure 4, absorption peaks at 1114 cm\(^{-1}\), 1257 cm\(^{-1}\), 1220 cm\(^{-1}\) - 1320 cm\(^{-1}\), 3318 cm\(^{-1}\), 1622 cm\(^{-1}\) and 2275 cm\(^{-1}\) can be observed for the neat PUF sample, which could be assigned to C-O-C, C-O from ester, C-N from amine group, N-H, \(-C=\text{C}\) and -NCO, respectively [9]. However, it can be seen in Figure 5 the flame retardant PUF sample containing DMMP has less and lower absorption peaks at high temperature range compared with the neat sample. This can be explained by the formation of the thick char layer covering the decomposed PUF substrate after the incorporation of the flame retardant containing phosphorus, which prevents the further thermal degradation of the sample in the high temperature and inhibits the release of some low molecular decomposed compounds into the gaseous phase during thermal degradation process of the flame retardant sample [10].

Figure 3. DTG curves of PU samples.

Figure 4. 3D and 2D TG-FTIR spectra of PU without DMMP.
In order to obtain more information about the pyrolysis product evolutions of the samples during heating, FTIR spectra of the neat PUF sample at the maximum evolution rates has been examined. FTIR spectra of the neat sample at 340 and 479°C are presented in figure 6. The characterized peaks at 2275cm⁻¹, 2352cm⁻¹, 3579cm⁻¹ and 1530cm⁻¹ can be observed in spectrum (a) [11], indicating the formation of some compounds containing -NCO, CO₂, H₂O and some products containing -NH from -NHC=O. It suggests the process of depolymerization at this temperature range, which could be caused by the break of the main chains in the PUF. In spectrum (b), the peaks at 1530cm⁻¹ and 2275cm⁻¹ have almost disappeared while some other peaks at 1513cm⁻¹, 2905cm⁻¹, 1465cm⁻¹, 1626cm⁻¹ and 935cm⁻¹ can be observed, which could be assigned to phenyl, -CH₃, -CH₂-, C=C and -CH₂- from alkene [12]. This indicates the thermal degradation of polyol and isocyanate, which are formed during the depolymerization of the PUF main chains. These results reveal that thermal degradation of the neat PUF can be described as two steps: the depolymerization of the main chains and the further pyrolysis of polyol and isocyanate. And thermal degradation of the neat PUF is presented in figure 7.

**Figure 5.** 3D and 2D TG-FTIR spectra of the flame retardant PUF sample with the DMMP concentration of 30%.

**Figure 6.** FTIR spectra of the neat PUF sample obtained at the maximal weight loss rates.
FTIR spectra of the flame retardant PUF sample at the maximum evolution rates of 163, 331 and 467°C are shown in figure 8. The absorption peaks of 2314 cm\(^{-1}\) and 1321 cm\(^{-1}\) can be observed for the flame retardant PUF in spectrum (a), which can be assigned to P-H and P=O \[13\]. It suggests that the compounds containing phosphorous groups could be released into the gaseous phase during the decomposition of flame retardant PUF. And the derivatives of these compounds could terminate the free radicals existing in the gaseous phase during combustion and reduce the flammability of materials. It also indicates that the flame retardant action of DMMP can be also detected in the gaseous phase at relative high temperature range \[14\]. In addition, as shown in figure 8, spectrum (b) and (c) are almost similar with spectrum (a). This phenomenon proves the inhibited thermal degradation of the underlying matrix, which may be due to the covering mechanism of the intumescent residual layer in high temperature.

The generated trends of water are shown in figure 9. It can be seen that the temperature of the maximum intensity peak is 364°C for the flame retardant PUF, which is 48°C lower than that for the neat PUF. This may be due to the decomposition of DMMP at the initial stage of combustion to form some phosphorus oxide and polyphosphorus acid, which could catalyze the dehydration reaction among polymer chains at the relative low temperature \[15, 16\]. The release of water could dilute the flammable gas in the gaseous phase and absorb the burning heat when subjected to the flame, which retards the thermal degradation of PUF and enhances its flame retardancy. However, the release of water for flame retardant PUF is inhibited obviously above 480°C while that for the near PUF remains
until 800 °C. It is possibly because the intumescent residual char layer covering the decomposed flame retardant PUF could inhibit the release of water and prevent the thermal degradation of the material further at higher temperature range, which can be also confirmed by the constant residual amount at the temperature range of 500-800 °C in TG curve of the sample (30% DMMP concentration) (Figure 2).

![Figure 9. Relationship between intensity and temperature for water.](image)

![Figure 10. Relationship between intensity and temperature for -NCO containing products.](image)

The generated trends of -NCO are shown in figure 10. The maximum intensity peak of -NCO for the flame retardant PUF sample can be observed in temperature range of 300-405 °C. And the highest maximum peak of -NCO for the neat PUF is at the same temperature range. However, it shows that the intensity of the maximum peak for the neat PUF is relatively higher than that for the flame retardant PUF sample. And the -NCO release from the neat sample could be detected until 800 °C compared to that from the flame retardant PUF. This implies that the thermal stability of the flame retardant PUF could be improved due to the covering mechanism of the intumescent residual layer on the substrate at higher temperature range. And the result reveals that the incorporation of DMMP could inhibit the release of some decomposed compounds containing -NCO in high temperature range, which could finally reduce the toxic hazard on people during the combustion of the PUF material.
4. Conclusions

Dimethyl methylphosphonate (DMMP) has been used as a flame retardant containing phosphorus 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 concentration and the P%. Thermal stability of the flame retardant sample can be enhanced at high temperature by forming the higher residual char covered on the decomposed PUF substrate at high temperature. Results from the LOI test and thermal analysis confirm the condensed flame retardant activity of DMMP for the flame retardant PUF sample. However, based on the information from TG-FTIR analysis, it can be concluded that although DMMP could improve the thermal stability of PUF samples by the formation of the 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 inhibited due to the presence of DMMP at high temperature.

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