Flame Retardancy of Thermoplastic Polyurethane Using Phosphorus-containing Flame Retardants

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Abstract. A new phosphorus-containing polymer was synthesized and applied as a flame retardant in the polyether thermoplastic polyurethane (TPU). This flame retardant combined with two commercial flame retardants of melamine pyrophosphate (MPP) and melamine cyanurate (MCA) were also used in TPU. Their flame retardancy, thermal degradation and structural feature were investigated by limiting oxygen index (LOI), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). The experimental data showed that the presence of phosphorus-containing flame retardant improve the limiting oxygen index, thermal stability and fire behavior. The LOI value of TPU including 20 wt% synthesized phosphorus-containing flame retardant and 20 wt% MCA was increased to 25.8. The thermal stability of TPU was also excellently improved comparing with the neat TPU. A maximum char residue was obtained when 20 wt% synthetic flame retardant and 20 wt% MPP were added into the TPU which the char yields were 18.7%. The combustion heat results showed that the value of neat TPU is highest than other TPUs by adding the different flame retardants. The SEM results showed that a dense char layer was obtained by adding the synthetic phosphorus-containing flame retardant and MCA with 20 wt % respectively into the TPU system.

1. Introduction
Thermoplastic Polyurethanes (TPUs) are consisted of alternating hard and soft segments, which belongs to the family of thermoplastic elastomers (TPE). As an important class of polymeric materials, TPUs have been widely used in coatings, films, binder, wire and cable for their excellent physical properties, chemical resistance, abrasion resistance, flexibility at low temperature, high strength, high elasticity and excellent stickiness [1-6]. For its organic flammability, it is necessary to increase flame retardancy in some application requiring high flame resistance, such as structural materials for aircrafts, construction industries, electronics and so on. Thus, the increased attention on safety requirements has accelerated the research on the flame-retardant TPU.

The flame-resistant polymers can be achieved by adding various flame-retardant additives into them. In the past decades, halogen-containing materials are widely used in TPU as effective flame retardants [7]. But the use of halogen-containing materials leads to serious environmental problems that they give rise to toxic and dense smoke during combusting [8]. In order to enhance the flame retardancy of polymers meanwhile to reduce environment pollution, enormous efforts have been made to explore the halogen-free flame retardants, such as inorganic materials [9-11], phosphorus-containing materials [12, 13], silicon-containing materials [14, 15], and so on. Pinto [9, 10] added two types of ATH (Aluminium hydroxide), with or without surface treatment, and mica to TPU to improve the flame resistance. Bourbigotet al [16] found that polyhedral oligomeric silsesquioxanes greatly improved the fire retardance of TPU. While the necessary amount of inorganic materials to
improve flame retardancy will lead to a sharp decrease in abrasion resistance and tensile strength. The silicon-containing materials were also getting bad comments for their poor water resistance and high cost. Comparing with those, the phosphorus-containing flame retardants demonstrate good capabilities in chemical stability, thermal stability, less toxic smoke and good flame-retardant properties for polymer composites as a promising substitution for halogen-free flame additives. Thus, much progress has been made to promote the flame retardancy of TPU using phosphorus-containing flame retardants. Richardson et al [17] used the Al salt of O-methyl P-methylphosphonic to increase the LOI of TPUs. But the small molecular phosphorous compounds might easily move out of the TPU for its poor consistency, which decrease the flame retardancy of polymer materials. So, great attentions were paid to phosphorus-containing polymer and great efforts were made on enhancing the flame retardancy of TPU. Schmelzer et al [18] used a combination containing an aromatic polyphosphonate, thus enabling a TPU to achieve a V-0 rating. Wang et al [19] synthesized the polyurethanes including different amounts of polybispropoxyphosphazene and used them as flame retardant in TPU.

In this work, a novel phosphorus-containing flame-retardant polymer was synthesized by a chain extender constituted with tris(3-hydroxypropyl)phosphine oxide (THPPO), phenylphosphinic acid (PPA) and 2-[(6-oxido-6H-dibenzo[c,e][1,2]oxaphosphinin-6-yl)methyl]butanedioic acid (DDP), polyethylene glycol 2000 (PEG2000) and diphenyl-methane-diisocyanate (MDI). The entire reaction process is the same as the composition of polyether thermoplastic polyurethane. The product is a polymer material and will not seriously damage the mechanical properties when it is added into the TPU. This new synthetic fire-retardant material and other two commercial products of melamine pyrophosphate (MPP) and melamine cyanurate (MCA) were added into the TPU with different mass fraction to check the flame retardancy. All the prepared samples were characterized by thermogravimetric analysis (TGA), scanning electron microscopic (SEM) and limiting oxygen index (LOI) measurements.

2. Experimental

2.1. Materials

Tris(3-hydroxypropyl)phosphine oxide (THPPO), Phenylphosphinic acid (PPA), 2-[(6-oxido-6H-dibenzo[c,e][1,2]oxaphosphinin-6-yl)methyl]butanedioic acid (DDP) and dimethyl formamide (DMF, analytical reagent) were kindly provided by TianJinLianKuan Fine Chemicals Co., China. Polyethylene glycol 2000 (PEG2000) and diphenyl-methane-diisocyanate (MDI) were obtained from Aladdin Reagent Co., Ltd. in China. Melamine pyrophosphate (MPP) and melamine cyanurate (MCA) were provided by Shian Co., Ltd., Shandong, China. Polyether thermoplastic polyurethane (TPU, WHT-8185) was provided by Yantai Wanhua Polyurethanes CO., LTD.

2.1.1. Synthesis of the Phosphorus-containing Flame Retardant. The synthesis of the phosphorus-containing flame retardant was performed with two-step esterification reaction of THPPO, PPA and DDP, and then the product was used as a chain extender, and it was combined with PEG2000 and MDI to generate a polymer by one-pot synthesis. The entire reaction process is shown in Scheme 1.
For a typical experiment, THPPO and PPA in a molar ratio of 1:1 were put into a 250mL three-necked flask equipped with a condenser and thermometer, and stirred 4 to 5h under vacuum conditions at 140°C. Appropriate DDP based on 1/2 molar ratios of -COOH and -OH were added into the reaction flask, and the temperature was raised to 175°C maintaining 1h. Then dried PEG was added to the reactor under atmosphere pressure to form the -OH terminated compound. This compound reacted with the MDI while the molar ratios of –NCO and –OH is 1.05:1, using DMF as the solvent at 75°C for 30 min. The product was poured into a plastic container, and aged for 10h at 120°C while evaporate the solvent (DMF). The product was washed by a molar ratio of 1:1 methanol and water. After drying under vacuum, it was grinded. Subsequently, a pale yellow powered solid was obtained, which is the phosphorus-containing flame-retardant polymer material, and it is called as TPDPM. The Fig.1 showed the FTIR (Perkin Elmer 400 spectrometer, Connecticut, USA) spectra of the TPDPM. FTIR (KBr) (cm⁻¹): 2857 and 2960 (-CH₂-), 3447 and 3316 (-CONH-), 1255 (P=O), 1061 and 958 (P-O-C), 1257 and 1163 (C-O-C), 1725 (C=O).

2.1.2 Preparation of Samples. The samples prepared by adding different mass fraction of TPDPM, MPP and MCA into the neat TPU were extruded by an extruder (CET 20, Kebeilong Keya, China).
The samples including flame retardants were recorded as FR-TPUs and were shown in Table 1. They were dried in an oven at 100°C for 2h before use.

2.2. Measurements

2.2.1. Flammability Evaluation. The LOI was measured by a XZT-100A oxygen index meter according to ASTM D2863. The sizes of the samples used for the test were 100.00 mm×6.5 mm×3.0 mm in dimension. Heat of combustion tests were carried out using a ZDHW-8 automatic calorimeter and selected several samples from FR-TPUs.

2.2.2 Thermogravimetric Analysis (TGA). The TGA data were performed in nitrogen atmosphere at a heating rate of 10°C /min using a SDT Q600 thermo gravimetric analyzer. In each case, a 3-5 mg sample was used to assess the thermal stabilities of specimens including the neat TPU, the synthetic fire retardant (TPDPM) and the various flame-retardant TPUs containing different content of flame retardants at the temperatures range from room temperature to 550°C.

2.2.3. Microstructure Analyses by SEM. Scanning electron microscopic (SEM) researches for the morphology of char residues absolutely combusted were made using S-4800 (Hitachi, Japan) scanning electron microscopy. The accelerating voltage was 20KV.

3. Results and Discussion

3.1. Flame Retardancy

The limiting oxygen index (LOI) [20] is a very important method to evaluate the flame retardancy of the polymer, which determines the ability of materials to be ignited. The burning behaviors of TPUs filled with TPDPM (20 wt%, 30 wt% and 40 wt%), MPP (0 wt%, 10 wt% and 20 wt%) and MCA (0 wt%, 10 wt% and 20 wt%) were characterized by the LOI. The LOI values of different specimens were presented in Table 1. It is very difficult to measure the LOI value of neat TPU because it melts very rapidly and the flame will not be terminated except for material absence [21]. The LOI values of FR-TPU1 and FR-TPU2 are approximate. The LOI values of FR-TPU4, FR-TPU5 and FR-TPU6 are also similar. Thus, the flame-retardant effects are very similar when added the same mass fraction of TPDPM to the TPU with or without other two commercial flame retardants. It indicates that the flame retardants (TPDPM) take great weight effect in enhancing the flame retardancy of TPU. The LOI value of the flame-retardant TPUs (FR-TPU9, FR-TPU10 and FR-TPU11) containing an equal flame retardant are different, and the value of FR-TPU11 is lowest. It can be seen, the flame-retardant effect of TPDPM is not better than other two commercial flame retardants when they were added into TPU as a single flame retardant. The LOI value of FR-TPU2 is 23.7 when the flame-retardant content was 30 wt% (20 wt% TPDPM and 10 wt% MCA). When the content of the TPDPM increased to 30 wt%, the LOI value of FR-TPU3 will increased to 25.1. For comparison, the LOI value of FR-TPU7 is 24.6 while 40 wt% TPDMP as a single flame retardant was added into neat TPU. It can be seen, TPDMP work together with other two kinds of flame retardants will have a better flame-retardant effect than TPDMP added alone into TPU. In addition, this formula reduces the cost because the two commercial flame retardants are very cheap. Furthermore, the LOI values of FR-TPU1, FR-TPU2, FR-TPU4 and FR-TPU5 show that the flame retardancy of TPUs by adding TPDPM and MCA are better than TPDPM and MPP.
Table 1. Formation of Samples and Results of LOI

|        | TPU (wt%) | TPDPM (wt%) | MPP (wt%) | MCA (wt%) | LOI (wt%) |
|--------|-----------|-------------|-----------|-----------|-----------|
| TPU    | 100       | 0           | 0         | 0         | Flammable |
| FR-TPU1| 70        | 20          | 10        | 0         | 23.5      |
| FR-TPU2| 70        | 20          | 0         | 10        | 23.7      |
| FR-TPU3| 60        | 30          | 0         | 10        | 25.1      |
| FR-TPU4| 60        | 20          | 20        | 0         | 25.5      |
| FR-TPU5| 60        | 20          | 0         | 20        | 25.8      |
| FR-TPU6| 60        | 20          | 10        | 10        | 25.3      |
| FR-TPU7| 60        | 40          | 0         | 0         | 24.6      |
| FR-TPU8| 70        | 30          | 0         | 0         | 23.2      |
| FR-TPU9| 80        | 0           | 0         | 20        | 22.7      |
| FR-TPU10| 80      | 0           | 20        | 0         | 22.3      |
| FR-TPU11| 80      | 20          | 0         | 0         | 21.9      |

The fire behaviors were also characterized by the heat releasing of combustion when the materials are completely burned. The continuous burning of ignited polymer materials depends on the heat balance of the combustion process. When the generated combustion heat is equal to or greater than the total heat required in the various stages of the combustion process, the combustion of the polymeric materials will proceed, otherwise it will be aborted or extinguished. Therefore, the less heat released in combusting, the more conducive to the fire resistance of the polymer materials was obtained. The combustion heat data of neat TPU and four FR-TPUs were showed in Table 3. The combustion heat value of neat TPU is higher than other FR-TPUs. It can be deduced that by adding the flame retardant to the neat TPU will reduce heat generation and improve the flame retardancy of the materials. In addition, the data of combustion heat of FR-TPU1 is highest and FR-TPU5 is lowest that compared with other flame-retardant TPU's. The results are consistent with the observed results of LOI that the heat of combustion is lowest while the LOI value is highest.

![Figure 1. FTIR spectra of the TPDPM](image-url)
Thermogravimetric analysis (TGA) is an effective method to evaluate thermal degradation and stability of materials [22, 23], and it is usually used to describe the decomposition rate and decomposition temperature of polymer. The thermal stability of TPDPM and FR-TPUs are evaluated by thermogravimetric analyzer. The 5% weight loss temperature ($T_{-5\text{ wt}\%}$), the 50% weight loss temperature ($T_{-50\text{ wt}\%}$) and the char yields are listed in Table 2.

The thermal decomposition curves of TPDPM in nitrogen are showed in Fig.2. The result reveals that the weight loss of TPDPM is 5 wt % when it is heated to 303°C. The mass loss rate maximizes at 410°C, the char residue is 14.52% when the temperature reaches 500°C.

Thermal stabilities of the neat TPU and flame-retardant TPUs were evaluated by TGA while the temperature range is from the room temperature to 550°C. The Fig.3 indicates the thermal degradation behaviors of the neat TPU and FR-TPUs in nitrogen atmosphere, and the data are listed in Table 2. As show in Fig.3, thermal degradation curve of neat TPU changes in two steps: the first step begins at about 280°C to produce the starting monomers with the depolymerisation of the urethane bonds; the second step begins at about 380°C, which indicates the bonds in the main chain, such as C-C and C-O, are further damaged [24]. The $T_{-5\text{ wt}\%}$ for FR-TPUs is lower than neat TPU, which due to the
interaction among TPU and flame retardants. The char yields of all the FR-TPUs are higher than neat TPU. It demonstrates that TPU by adding the flame retardants will increase char residues yield because phosphorus-containing flame retardants contribute to promoting the char yields of materials, especial oxygen polymer. In addition, the char yields of the FR-TPU1 and FR-TPU4 are much more than the rests of FR-TPUs. It is because MPP has the high phosphorus content as well as facilitate the char yields. This result indicates that the char residues of FR-TPUs with different proportions of TPDPM and MPP are more than those samples with TPDPM and MCA.

The Fig.4 shows the thermal degradation behaviors of the neat TPU, the three flame-retardant TPUs containing 20wt% TPDPM, 20wt% MPPand 20wt% MCA in nitrogen atmosphere, and the data are also listed in Table 2.

| Table 3. The data of combustion heat |
|-------------------------------------|
| TPU  | FR- TPU1 | FR- TPU4 | FR- TPU5 | FR- TPU6 |
|------|----------|----------|----------|----------|
| 32052| 31299    | 28879    | 28473    | 28982    |

3.3. Morphology and Structure of the Char Residues

In Fig.5, the SEM images of the char residues for FR-TPU1, FR-TPU4, FR-TPU5 and FR-TPU6 at 5000 times magnification are presented. Based on SEM, the morphologies of the residues of the four FR-TPUs have the different images. It is apparent fact that FR-TPU1 and FR-TPU6 have greater pore structure compared with FR-TPU4 and FR-TPU5. The pore structure contributes to gas diffusion and heat transfer, and it makes the materials burn readily. From the results, when 20 wt% of TPDPM and MPP or MCA were added to the TPU, the char residues have the more compact structure and this structure is capable of providing a preferable physical barrier to prevent thermal transmission and spread of the combustible gases. The SEM micrographs of the char residues indicated that the flame retardants of both 20 wt % TPDPM and MPP or MCA are beneficial to improve the flame retardancy of TPU.

Figure 3. TG curves of neat TPU and FR-TPUs

Figure 4. TG curves of neat TPU, 20TPDPM-TPU, 20MPP-TPU and 20MCA-TPU
Figure 5. SEM micrographs of residual chars for FR-TPUs after combustion

4. Conclusion
A phosphorus-containing flame-retardant material was synthesized through a three-step reaction and was characterized by FTIR. The FTIR results confirm this successful synthesis. Several tests were using to characterize the flame retardancy and thermal stability of the systems. The LOI measurements indicate that the samples with 20 wt% TPDPM and 20 wt% MCA in the TPU show the highest LOI value, and the heat of combustion data also proved the same consequence. The TGA results indicate that the synthesized flame retardant is benefit to the char residues formation of the TPU. The char residues are higher than other FR-TPUs by adding the TPDPM and MPP into the TPU.

5. References
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