# Preparation of Reactive and Additive Flame Retardant with Different Oxidation State of Phosphorus on the Thermal and Flammability of Thermoplastic Polyurethane

**Fei Lin[1], Haizhen Lin[2, 3], Junmu Ke[2, 3], Jingling Liu[2, 3], Xin Bai[2, 3], Denglong Chen[1, 2, 3, *]**

[1]College of Environmental Science and Engineering, Fujian Normal University, Fuzhou, China

[2]Quangang Petrochemical Research Institute, Fujian Normal University, Quanzhou, China

[3]Fujian Environmental Friendly Polymer Material Innovation Center, Quanzhou, China

**Email address:**
1050085845@qq.com (Fei Lin), lhz233@163.com (Haizhen Lin), 15705913884@163.com (Junmu Ke),
jingling503@163.com (Jingling Liu), bai.xin@foxmail.com (Xin Bai), chendenglong@163.com (Denglong Chen)
*Corresponding author

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**Abstract:** A novel phosphorus-nitrogen flame retardant polyols (FRPE) was synthesized from condensation reaction with adipic acid (AA), ethylene glycol (MEG), diethylene glycol (DEG), maleic acid (MA), 9, 10-dihydro‐9‐oxa‐10‐phosphaphenanthrene‐10‐oxide (DOPO) and tris (2-hydroxyethyl) isocyanurate (THEIC) as raw materials. The structure of FRPE was characterized by Fourier transform infrared spectrometry (FTIR)，thermogravimetric analysis (TG) and Gel permeation chromatography (GPC). FRPE was used as a flame retardant in the preparation of thermoplastic polyurethanes (TPU). The effects of FRPE on the mechanical, thermal, and flame retardant properties of TPU were investigated. The another aim of this study is an investigation of the effect of different oxidation state of phosphorus in phosphorus-based flame retardants on the thermal and flame retardant properties of TPU. Three different oxidation states of phosphorus (triphenylphosphite (TPPI) (+3), triphenylphosphate (TPP) (+5), and FRPE (+1)), with different thermal stabilities at a constant phosphorus content (0.8 wt%) have been utilized. Thermal and flame retardant properties were evaluated by TGA and cone calorimetry test (CCT), respectively. the surface morphology of char residue after CCT was observed by scanning electron microscopy (SEM). the flame-retardant mechanism of these three flame retardant were investigation by FTIR-TG. The result show that the flame retardant properties of TPU composites were significantly improved, and the flame retardant mechanism of different oxidation state phosphorus flame retardants are presented.

**Keywords:** Polyol, Thermoplastic Polyurethane, Flame Retardant, Combustion, Pyrolysis

## 1. Introduction

Thermoplastic polyurethanes (TPU) is the addition product of polyols, polyisocyanate and chain extender. With its good hardness, chemical corrosion resistance and mechanical properties, inparticular it's excellent elasticity, hence, TPU has been widely used in a broad range of applications, such as, leather wear, shoes, cable, automobile parts, etc. However, like most polymers, TPU has low level of thermal performance due to it's organic structure, which restricts its application in many other fields where flame-retardant properties are desired. In recent years, the enhancement of TPU's flame retardant property has drawn much attention. Therefore, it is essential and imperative to develop flame-retardant TPU to reduce the risk of fire.

In order to endow TPU with good flame retardancy, its achieved through the use of additive type flame retardants negatively affects the mechanical properties of TPU [1-4]. Moreover, like halogenated flame retardants will generate toxic substances and corrosive gases and smoke during combustion and high temperature processing [5-7], which led to concerns about the exposure to halogen-containing contaminants, and in turn stimulated the development of

reactive-type flame retardants. Generally, the application of reactive type flame retardants involves the design and modification of polyols with different chemical structures. Therefore, various phosphorus-containing reactive-type flame retardants have been developed to substitute addtive flame retardants [8-12]. Typically, 9, 10-dihydro‑9‑oxa‑10‑phosphaphenanthrene‑10‑oxide (DOPO) was found to exhibit an outstanding performance as a reactive-type flame retardant in diverse polymers due to its higher thermal stability and better flame retardancy [13-14]. Recently, some studies have indicated that flame retardant efficiency is significantly enhanced when both phosphorus and nitrogen were presented in the polymers due to the synergistic effect between phosphorus and nitrogen [15-18]. However, there are rarely used for TPU. What's more, there are less reports describe the effect of oxidation state of phosphorus on the properties of TPU. Although DOPO has excellent flame retardant efficiency in many polymers, the chemical environment around the phosphorus atom has a crucial influence on the flame retardant properties, thus the flame retardancy mechanism of DOPO in various polymers is different. Hence the flame retardant efficiency and mechanism of DOPO associated with the characteristic of polymer need to be further studied.

In this study, a novel flame retardant polyols (FRPE) containing phosphorus and nitrogen was synthesized in one-pot, characterized and used for TPU, and three different oxidation states of phosphorus, TPPI (+3), TPP (+5), and FRPE (+1), are studied in TPU at 0.8wt.% phosphorus. Molecular weight of novel polyols was characterized by GPC, the flame retardancy and thermal properties of TPU were characterized by LOI, UL 94-V, CCT and TG, the char layer of TPU after CCT was characterized by digital photos, SEM, and FTIR spectra, which deduced the flame retardant mechanism of TPPI (+3), TPP (+5), and FRPE (+1) in TPU composites, further more, the corresponding flame retarding mechanisms of the above three different flame retardant in TPU matrices were carefully discussed by FTIR-TG.

# 2. Experimental

## 2.1. Material

9, 10-dihydro‑9‑oxa‑10‑phosphaphenanthrene‑10‑oxide (DOPO, P content 6.97%) was supplied by Decheng Industry Co., Ltd., China. Trihydroxyethyl isocyanurate was acquired from Dahua Weiye Pharmecutical and Chemical Co., Ltd., China, adipic acid (AA), ethylene glycol (MEG), diEthylene Glycol (DEG), Maleic acid (MA), triphenylphosphite (TPPI, P content 10%), triphenylphosphate (TPP, P content 9.5%), Polyadipic acid 1, 4-butanediol polyols (7020, Mn=2000), N, N-dimethylformamide (DMF) are all purchased from Aladdin Co., Ltd., Diphenylmethane diisocyanate (MDI) was purchased from Wanhua Chemical Group Co., Ltd., Shangdong, China.

## 2.2. Synthesis of FRPE

DOPO (70 g 0.325mol) and diethylene glycol (114g 1.075mol) were placed in four flasks with agitator, condensation tube and thermometer, under a 80°C oil bath, and then maleic acid (41.5 g 0.36 mol) was added into the flask within two hours, subsequently, the addition reaction between P−H bond in DOPO and C=C bond in MA proceeded fully under a 80°C oil bath for 24 h. and then adipic acid (76 g 0.52mol) was added into the flask and the temperature was raised to 120°C and maintained for 4 hours, and control the temperature of distillation column at 80-90°C, so that the generated water was steamed out gradually and controlled. after that, the temperature head to 150°C gradually, finally, Theic (43g 0.165mol) was added, the temperature head to 220°C gradually. When the fractionation column is no longer effluent. The vacuum is pumped in stages until the acid value is below 2 mg NaOH/g. The reaction is stopped and the product is obtained.

## 2.3. Preparation of Sample

The synthesized polyols with phosphorus and nitrogen was incorporated into TPU as a reactive flame retardant, combining it with commercial polyester polyols 7020. The flame retardant thermoplastic polyurethanes were prepared by a three-step method. At first the calculated quantity of polyols and diphenylmethane diisocyanate were added into three neck round bottom flask equipped with a mechanical stirrer, thermometer and provision for nitrogen flushing. The temperature was maintained at 75°C with continued stirring and continuous nitrogen for 2 hours. Adjusting the system's viscosity with DMF. Secondly, added addictive flame retardants (TPPI and TPP, 0.8wt.% phosphorus content) were homogenously mixed with a mechanical stirrer for 1 hour. Finally, the resultant mixture was poured into the teflon mold, allowed to cure at 80°C in oven for 48 h.

## 2.4. Measurements

### 2.4.1. Gel permeation Chromatography (GPC)

The synthesized polyols were analyzed using standard characterization techniques. Gel permeation chromatography (GPC) was used to determine the molecular weight of the sample. GPC system by Waters (Milford, MA), USA (column: mixed PL gel 300 × 718 mm, 25μm) Tetrahydrofuran was used as eluent solvent at a flow rate of 1 ml/min at 30°C.

### 2.4.2. Thermal Gravimetric Analysis (TG)

Thermal gravimetric analysis was conducted on a TGA thermal analyzer (Waters TGA Q50). A sample of about 10 mg was put in a silica pan to evaluate the thermal stability of the sample. The sample was heated at a heating rate of 10°C /min from ambient temperature to 700°C.

### 2.4.3. Fire Testing

Two standard test methods were utilized to evaluate the flame retardancy of the composites. LOI is an indicator of the minimum oxygen concentration that is needed to cause combustion of the

material in an oxygen-nitrogen atmosphere through downward burning of a vertically mounted specimen. The test specimen is 70-150 mm in length, 6.5 mm in width and 3 mm in thickness. The LOI test of specimens were proceed according to the Chinese Standard GB/T 2406-93, using a JF-3 instrument (Jiangning Analyzer Plant, China). For the vertical fire test of specimens (125 mm×13 mm×3mm), according to the Chinese Standard GB/T 2408-1996, by using a CZF-3 instrument (Jiangning Analyzer Plant, China), there are three ratings: V-0, V-1 and V-2. If the total flame time is less than 10s, the sample is assigned a V-0 rating. When the total flame time is between 10 and 30 s, and the cotton under the sample cannot be set on fire by the burning drops, the sample is assigned a V-1 rating. However, if the cotton catches fire, the sample can only be assigned a V-2 rating. V-0 stands for the best rating. At least five specimens were used in each experiment.

### 2.4.4. Cone Calorimeter Test

Cone calorimeter test is an instrument to evaluate the flame retardancy of composites. The cone calorimeter manufactured by FTT Limited of the United Kingdom uses a truncated conical heater element to irradiate the test specimen with heat fluxes from 10 to 100 kW/m$^2$ simulating a range of fire intensities. In the present work, the cone calorimeter tests were carried out according to ISO 5660-1: 2002, using an incident heat flux of 35 kW/m$^2$ and heated to 750°C. The bottom and edges of each 100 mm×100 mm×3 mm specimen were wrapped with an aluminium foil. The measured parameters were time of ignition (TTI), peak heat release rate (PHRR), mean heat release rate (MHRR), total heat evolved (THE), total heat evolved/ total mass loss (THE/TML), CO yield, total smoke release (TSR) and residual mass. The heat released was calculated from the consumption of oxygen during combustion. The values of the listed parameters can be reproduced to within 10%.

### 2.4.5. Scanning Electron Microscopy (SEM)

In order to determine the effect of the structure of char on the flame retardancy of TPP, TPPI and FRPE, the char residues after the cone calorimeter tests at 750°C were observed by regulus 5100 scanning electron microscope (Hitachi, Japan).

### 2.4.6. Fourier Transform Infrared

Fourier transform infrared (FTIR) spectra were obtained by a Nicolet 10 spectrometer (Nicolet Instrument Company, U.S.A.) using KBr pellets. The wave number range was 500−4000 cm$^{-1}$.
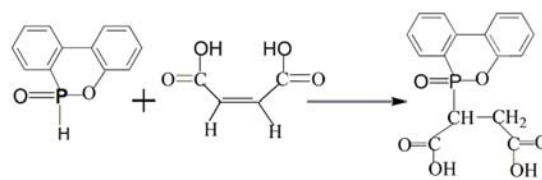
### 2.4.7. TG–FTIR Analysis

The TGA–FTIR analysis was performed using a Waters TGA Q50 coupled to a Nicolet is10 FTIR to study the thermal decomposition of the flame retarded samples. The analyses were conducted under a nitrogen atmosphere (flow rate 20 ml/min) at a heating rate of 10°C /min over a temperature range of 30–700°C. The sample weight was around 8mg. The coupling system between the TG and FTIR was maintained at 250°C to prevent condensation of the evolved gases.
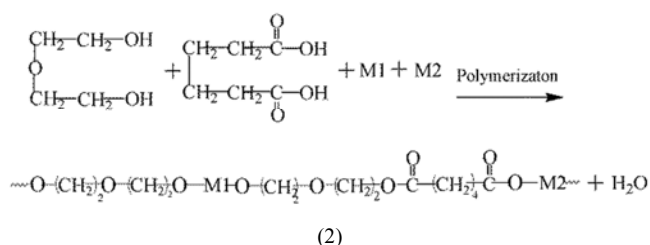
## 3. Results and Discussion

### 3.1. Characteristics of FRPE

### 3.1.1. Reaction Mechanism of Synthesis of FRPE

There are two main reactions in the synthesis of FRPE: (1) the addition reaction between the P-H bond on DOPO and the unsaturated double bond on Maleic acid; (2) the esterification polycondensation reaction between hydroxyl group and carboxyl group, as shown in Formula (1) and Formula (2).



(1) DOPOMA



(2)

**Figure 1.** *Synthesis route of FRPE.*

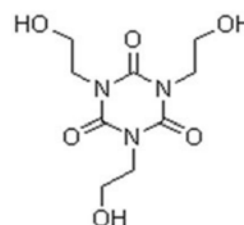In formula (2), M2 is tri (2-hydroxyethyl) isocyanurate (THEIC):



**Figure 2.** *THEIC.*

### 3.1.2. Infrared Spectrum Characterization of FRPE

The infrared spectra of DOPO, DOPOMA and polyester polyols with phosphorus and nitrogen in structure are shown in Figure 3.
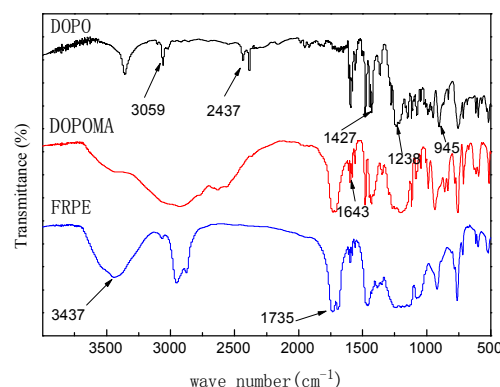


**Figure 3.** *FTIR spectrum of DOPO, DOPOMA and FRPE.*

The characteristic absorption peaks of P-H bond at 2437 cm$^{-1}$ and C=C bond at 1643 cm$^{-1}$ for maleic acid can be seen from lines DOPO and DOPOMA. The characteristic absorption peaks of C=C bond disappear in the infrared spectra of DOPOMA. In addition, the characteristic absorption peaks of P-O-C at 945 cm$^{-1}$, P=O at 1238 cm$^{-1}$, P-C at 1427 cm$^{-1}$, and the wide absorption peaks of -COOH in maleic acid molecule in the range of ~3000 cm$^{-1}$ appear in the spectra of DOPOMA. This indicates that the P-H bond in DOPO reacts with the C=C bond of maleic acid to form DOPOMA. From line FRPE of Figure 3, it can be seen that the broad absorption peak of -COOH in maleic acid molecule in the range of ~3000 cm$^{-1}$ narrows in the infrared spectrum of polyester polyols with phosphorus and nitrogen in structure; the characteristic absorption peak of -OH in the range of 3400-3500 cm$^{-1}$ appears, and the carbon group (C=O) stretching vibration absorption peak of ester is around 1735 cm$^{-1}$, which is the result of the reaction of -OH in diethylene glycol and THEIC with -COOH in DOPOMA molecule. That is to say, they all characterize the basic chemical structure of polyester polyols with phosphorus and nitrogen containing.

### 3.1.3. Gel Permeation Chromatography Characterization of FRPE

Gel permeation chromatography of polyester polyols with phosphorus and nitrogen in structure is shown in Figure 4. The Mw and Mn of the polyester polyols with phosphorus and nitrogen in structure were 1070 and 839 respectively, and the molecular weight distribution index D was 1.28. While there was only a single peak 932 in the polyester polyols spectra.

This result indicated the addition reaction between DOPO and MA, the esterification polycondensation reaction between hydroxyl group and carboxyl group had occurred.
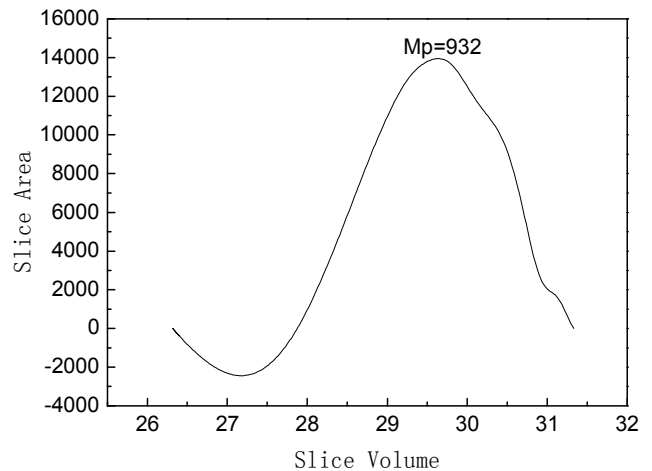


**Figure 4.** *GPC curve of polyester polyols with phosphorus and nitrogen in structure.*

### 3.1.4. Thermal Properties of FRPE

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) were used to test the thermal properties of polyester polyols with phosphorus and nitrogen in structure. The results are shown in figure 5.
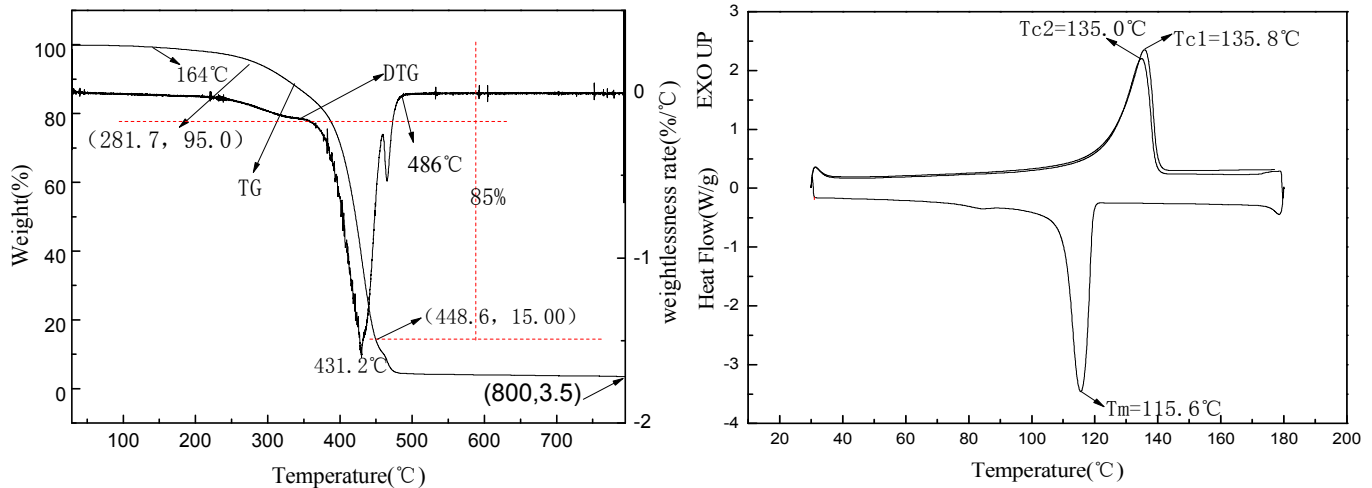


**Figure 5.** *DSC and TG-DTG curve of polyester polyols with phosphorus and nitrogen containing.*

Figure 5 shows that the melting peaks of phosphorus-nitrogen polyester polyols appear when heated to 115.6°C. The peaks are narrow and sharp, and the curves on both sides are smooth, so it can be concluded that the synthesized products have high purity. The first cooling crystallization temperature of the polyester polyols is 135.8°C, and the second melting cooling crystallization temperature is 135°C. TG-DTG curves show that the initial decomposition temperature of polyester polyols with phosphorus and nitrogen in structure is 164°C, the maximum weight loss rate

temperature is 431.2°C, the temperature is 281.7°C when the thermal weight loss is 5%, the temperature is 448.6°C when the weight loss is 85%, and the carbon residue rate is 3.5% at 800°C. The common DOPO flame retardant intermediates lose 90.8% of their weight at 213-427°C and the common organophosphorus flame retardants such as triphenyl phosphate lose 98% of their weight at 320°C [19]. Compared with the common DOPO flame retardant intermediates, polyester polyols containing phosphorus and nitrogen have higher thermal stability and charring properties.

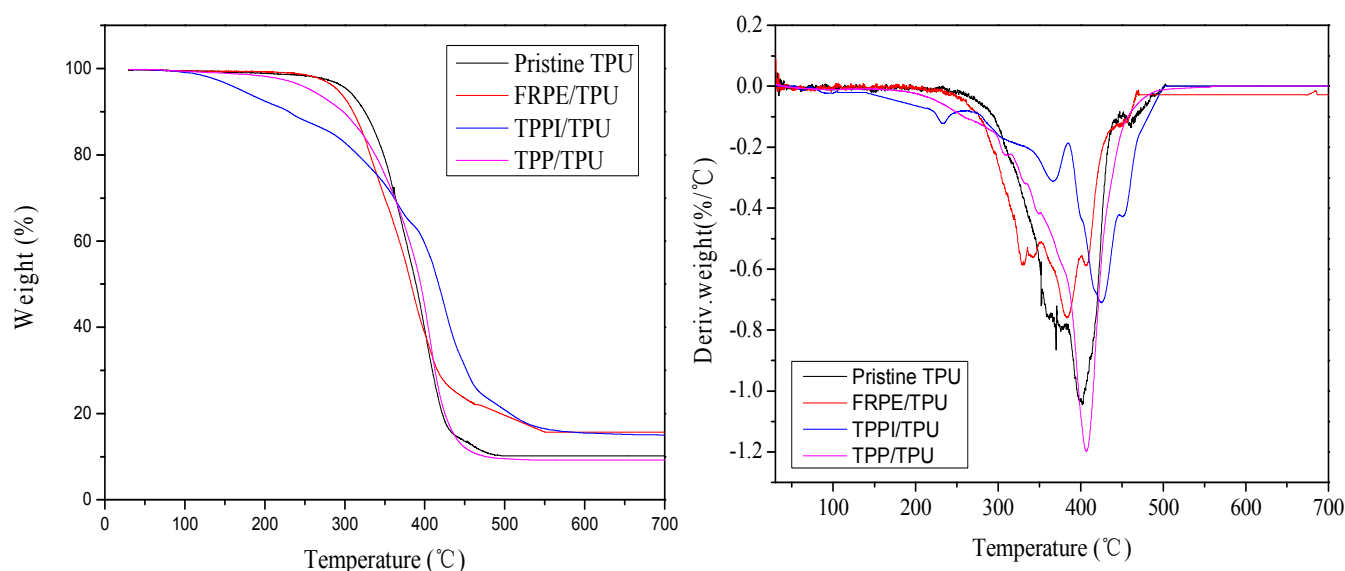## 3.2. Thermo Gravimetric Analysis (TG and DTG) of TPU



**Figure 6.** *The TGA and DTG spectra of pristine TPU and flame retarded TPU.*

Thermogravimetry analysis (TG) method is applied to investigate the thermal degradation behaviors of the sample by measuring the volatilization of degradation products. Figure 6 shows the TG/DTG profile of PU filled with different oxidation state phosphorus flame retardant. And the corresponding characteristic values are listed in table 1. Pristine TPU shows a two step degradation processes, the degradation steps of PU take place in the temperature ranges at 258-384°C and 384-506°C, respectively. The 5% weight loss of pristine TPU occured at 303.7°C with the maximum mass loss rate at 370.4°C ($T_{max1}$) and 400°C ($T_{max2}$) in the two decomposition stage, respectively, which was ascribed to the depolymerzation of the chain of urethane and the formation of isocyanate, alcohol, primary and/or secondary amine, olefin as well as crbon dioxide in the frist decomposition and The second degradation process corresponds to the thermal decomposition of the soft segment, the residued of pristine at 700°C was 8.08%.

The thermal decomposition process of FRPE/TPU was characterized by two main stages as well, and the corresponding temperature ranges at 237.8-352.1°C and 352.1-498.3°C, respectively. By comparing with those of

pristine TPU, the $T_{5wt\%}$ and $T_{max1}$ values of flame retarded TPUs were shifted to lower values, indicating these phosphorus-containning designs were thermally less stable than pristine thermoplastic polyurethanes, except the $T_{max1}$ values of TPP/TPU was higher than pristine TPU, that's why the residue of TPP/TPU is lower than pristine TPU. The thermal decomposition process of TPPI/TPU was characterized by three main stage, the first stage is due to the decomposition of phosphorus-containing moieties in the temperature range of and 139.7-253.8°C with a DTG peak at 233.4°C. Whereas the second stage can be attributed to the decomposition of unstable urethane groups in the temperature range of 253.8-384.1°C with a DTG peak at 365.8°C. And the third stage maybe the destroy of char residue and the decomposition of soft segment in high temperature at range of 343.4-570.6°C with a DTG peak at 425.2°C, respectively. These three flame retardant TPU have 14.83%, 14.79% and 8.00% char residue, respectively. It's obvious that the higher oxidation state of phosphorus showed poorer flame retardant properties than the lower oxidation state and with an increase in the oxidation state of phosphorus, the amount of char formation increases [20].

**Table 1.** *Thermal properties of pristine TPU and flame-retarded TPUs.*

| | $T_{5wt\%}$ (°C) | $T_{max1}$ (°C) | $T_{max2}$ (°C) | $T_{max3}$ (°C) | $R_{Tmax1}$ (%/min) | $R_{Tmax2}$ (%/min) | $R_{Tmax3}$ (%/min) | $C^{700}$ (wt%) |
|---|---|---|---|---|---|---|---|---|
| Pristine TPU | 303.7 | 370.3 | 400 | — | 0.79 | 1.04 | — | 8.08 |
| FRPE/TPU | 291.7 | 329.3 | 384.1 | — | 0.58 | 0.75 | — | 14.83 |
| TPPI/TPU | 170.2 | 233.4 | 365.8 | 425.2 | 0.13 | 0.31 | 0.71 | 14.79 |
| TPP/TPU | 261.8 | 413.3 | — | — | 1.23 | — | — | 8.00 |

## 3.3. Flame Retardance and Combustion Behaviors

LOI test is one of the most useful tools to evaluate whether the materials are flame-retarded in air. The influence of incorporation of the flame retardant on the LOI values of TPU

was investigated. As presented in Table 2, the LOI value of pristine TPU was as low as 20%. It is easily ignited and burns rapidly after ignition. Finally, it burns out without trace and the smoke and melt dripping were very serious. Incorporation of FRPE or additive segments changed this situation, the fire

finally self-extinguished even with a low content of 0.8% P or 0.57% N. It is clearly showed that the addition of FRPE, TPP and TPPI enhance the LOI value. When incorporating 0.8% P or 0.57% N into TPU, the LOI value of FRPE/TPU, TPP/TPU and TPPI/TPU have been increased to 28%, 25%, 25%, respectively.

*Table 2. Mechanical and flame retardant properties of pristine and flame retarded TPUs.*

|  | UL-94 | LOI | tensile strength (Mpa) | elongation at break (%) |
|---|---|---|---|---|
| Pristine TPU | V-2 | 20 | 5.0 | 1563.5 |
| FRPE/TPU | V-0 | 28 | 3.7 | 1330.2 |
| TPPI/TPU | V-1 | 25 | 4.6 | 1514.3 |
| TPP/TPU | V-1 | 25 | 4.4 | 1501.0 |

To further evaluate the flammability behavior of TPU, cone calorimeter tests were performed for pristine TPU, TPPI/TPU, TPP/TPU and FRPE/TPU. Cone calorimeter is able to bring quantitative analysis to the flammability of materials by investigation parameters such as the peak heat release rate (PHRR), the heat release rate (HRR), the total heat release (THR), the time to ignition (TTI), the total smoke production (TSP), and the average mass loss rate (Av-MLR).

The HRR and THR curves of pristine and flame retarded TPU filled with different oxidation state phosphorus flame retardants are shown in figure 7 and the corresponding cone data are presented in table 3. Flame retarded samples showed prior and lower HRR compared to the pristine TPU. The earlier HRR of flame retarded samples is due to the lower thermal stability of the flame retardants. The HRR of TPU is significantly decreased upon addition of FRPE, It is likely that the formation of a large amount of char residue during burning, as shown in Figure 8, accounts for the greater flame resistance of TPU. TPP/TPU sample show lower HRR with prolonged burning behavior as compared to the other flame retardants and the pristine sample. FRPE displays greater reduction of peak HRR of TPU compared to other flame retardants, indicate that FRPE is a better flame retardant to improve the flame retardancy of TPU. FRPE shows better flame resistance and lower AMLR with TPU compared to other flame retardant. All filled samples show low THR compared to the pristine sample.

It was observed that pristine TPU burns rapidly and its PHRR was 459.31 kw/m$^2$, however, the PHRR values of FRPE/TPU, TPPI/TPU and TPP/TPU were 228.93 kw/m$^2$, 292.86 kw/m$^2$ and 404.16 kw/m$^2$ with reduction of 50.15%, 36.24% and 12.00% compared with that of pristine TPU. The THR value for pristine reached 36.86 MJ/m$^2$, while the THR values of FRPE/TPU and TPPI/TPU declined to 13.31 MJ/m$^2$ and 15.21 MJ/m$^2$, respectively. The reduction of the HRR and THR values are likely attributable to char formation promoted by FRPE and TPPI, which slows heat and mass transfer between the gas and condensed phases (as shown in figure 8). But the THR values of TPP/TPU was 35.97 MJ/m$^2$, only reduce 2.41% compared with that of pristine TPU.

These important parameters are summarized in Table 3 based on the heat release rate (HRR) and total heat release (THR) curves of the CCT (Figure 7). Pristine TPU was easy to be ignited and burns out rapidly after ignition. Therefore, the highest values of PHRR and THR of pristine TPU were obtained with a few residue left. Compared with pristine TPU, the TTI values increased to 51s and 54s for TPP/TPU and FRPE/TPU, respectively. However, the TTI value of TPPI/TPU decrease to 29s due to the low thermal ability of TPPI. Furthermore, incorporating FRPE and TPPI into TPU decreased the THR values to 13.31 MJ/m$^2$ (−63.9%), 15.21 MJ/m$^2$ (−53.7%), respectively. However, the THR values of TPP/TPU almost equal to pristine TPU, decreased to 35.97 MJ/m$^2$ (−2.4%). The time to ignition (TTI) is an important flame retardant parameter for materials. The TTI of flame retarded TPUs are earlier by 10s, 14s and 13s than pristine TPU, respectively. The reduction of TTI may be due to the lower thermal stability of P-O-C and P-C bonds in TPPI, FRPE, and TPP, leading to accelerate thermal decomposition of TPU after irradiation, the phenomenon is suggested by TG. The Av-MLRs of FRPE/TPU, TPPI/TPU and TPP/TPU were 0.025 g/s, 0.032 g/s, and 0.044 g/s, respectively. The Av-MLR of pristine TPU was 0.042 g/s, higher than the other three samples. This phenomenon demonstrates that FRPE, TPP and TPPI play key roles in the condensed phase. It is obvious that FRPE/TPU had the lowest TSP among all of the TPUs. The lower TSP is one of the important characteristics of the flame- retardant TPU. As can be seen from table 3, FRPE, TPP and TPPI have the best performance to reduce the TSP values of TPU. It is benefit from these flame retardant could form carbon residue at the surface of TPU, which could efficiently hamper the transfer of heat and oxygen, resulting in retarding the smoke release of samples.

The analyzing of the results data from the CCT demonstrated that the FRPE could greatly improve the flame retardancy of TPU, meanwhile, it is evident that FRPE and TPPI play key roles in the condensed phase.
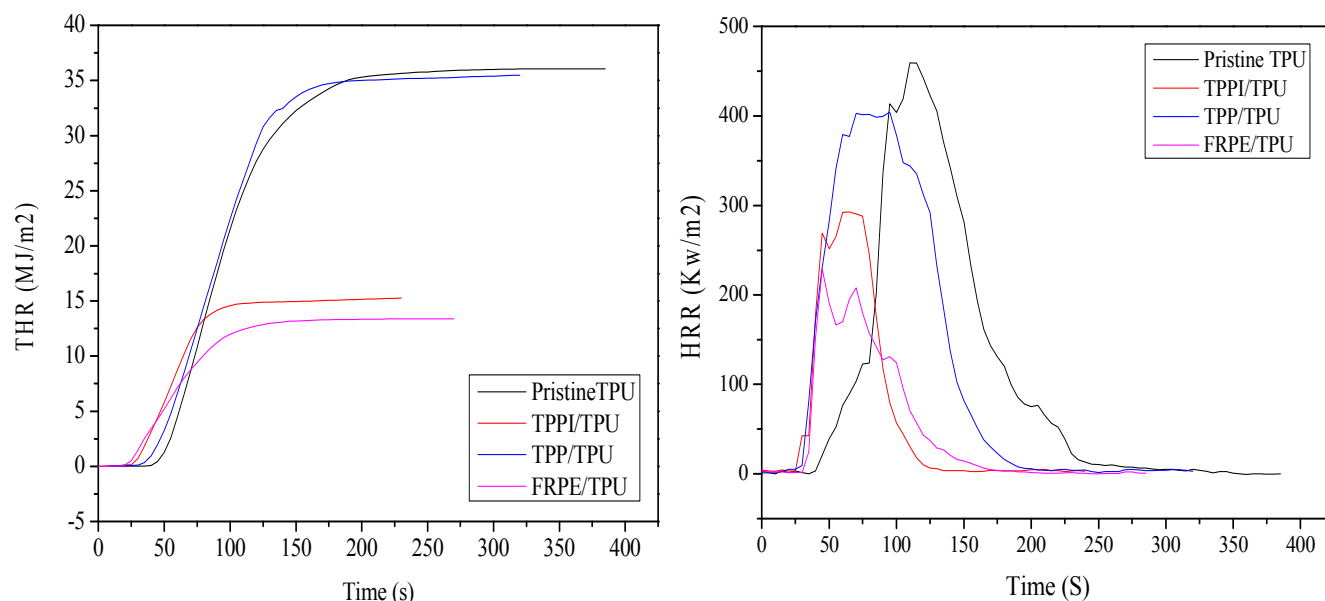
**Figure 7.** *The HRR and THR curves of pristine and flame retarded TPUs.*

**Table 3.** *Cone calorimeter test data of pristine and flame retarded TPUs.*

| sample | PHRR (kw/m$^2$) | THR (MJ/m$^2$) | TTI (s) | TSP (m$^2$) | Av-MLR (g/s) |
|---|---|---|---|---|---|
| Pristine TPU | 459.31 | 36.86 | 43 | 6.34 | 0.042 |
| FRPE/TPU | 228.93 | 13.31 | 33 | 3.67 | 0.025 |
| TPPI/TPU | 292.86 | 15.21 | 29 | 3.69 | 0.032 |
| TPP/TPU | 404.16 | 35.97 | 30 | 5.53 | 0.038 |

Figure 8 shows the digital photos of fire residues. At the end of the cone calorimeter test, as the figure 8 shown, It is obvious that the pristine TPU specimen has the lowest left while other specimens produce some black fire residues. Figure 9 illustrates the surface and inside micromorphology of fire residues. The morphology of low times (30-150) magnification reveals that pristine TPU formed loose char layer with a lot of micro holes, which cannot stop further degradation of the inside. Compared with pristine TPU, there are few or no holes on the surface of other TPU carbon layers containing flame retardant elements such as phosphorus or nitrogen, while there are arched bubbles on the surface of flame retarded TPU carbon layers. This is due to the existence of phosphorus element. During combustion, the bonds break to form phosphoric acid, metaphosphatic acid and polymetaphosphatic acid to form a mucous film, which can protect the inside TPU materials and prevent flammable gases from escaping from inside. The formation of arched bubble film, play a role in preventing the exchange of mass and heat between the substrate and air.

The morphology of higher magnification shows that there are amount of particles distributed on the carbonized layer. And in the surface of arched bubbles, there are white substance on the surface, these substance might be salts or esters of phosphoric acid and polyphosphoric acid which dehydrate the polymer chains to form carbonized layer.
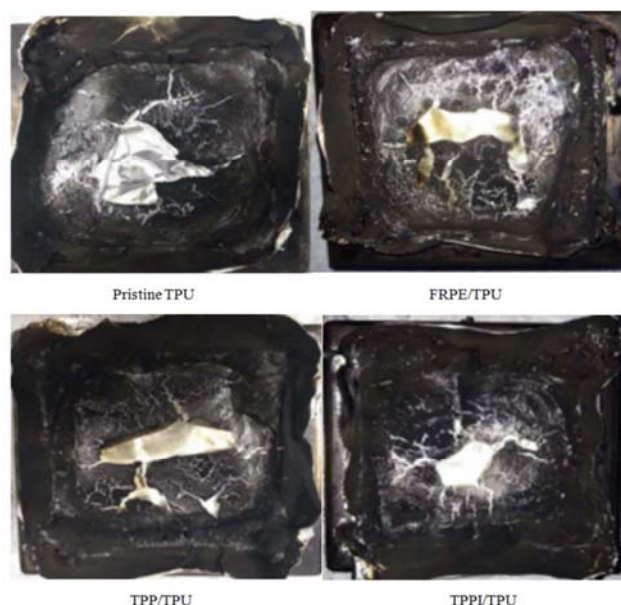


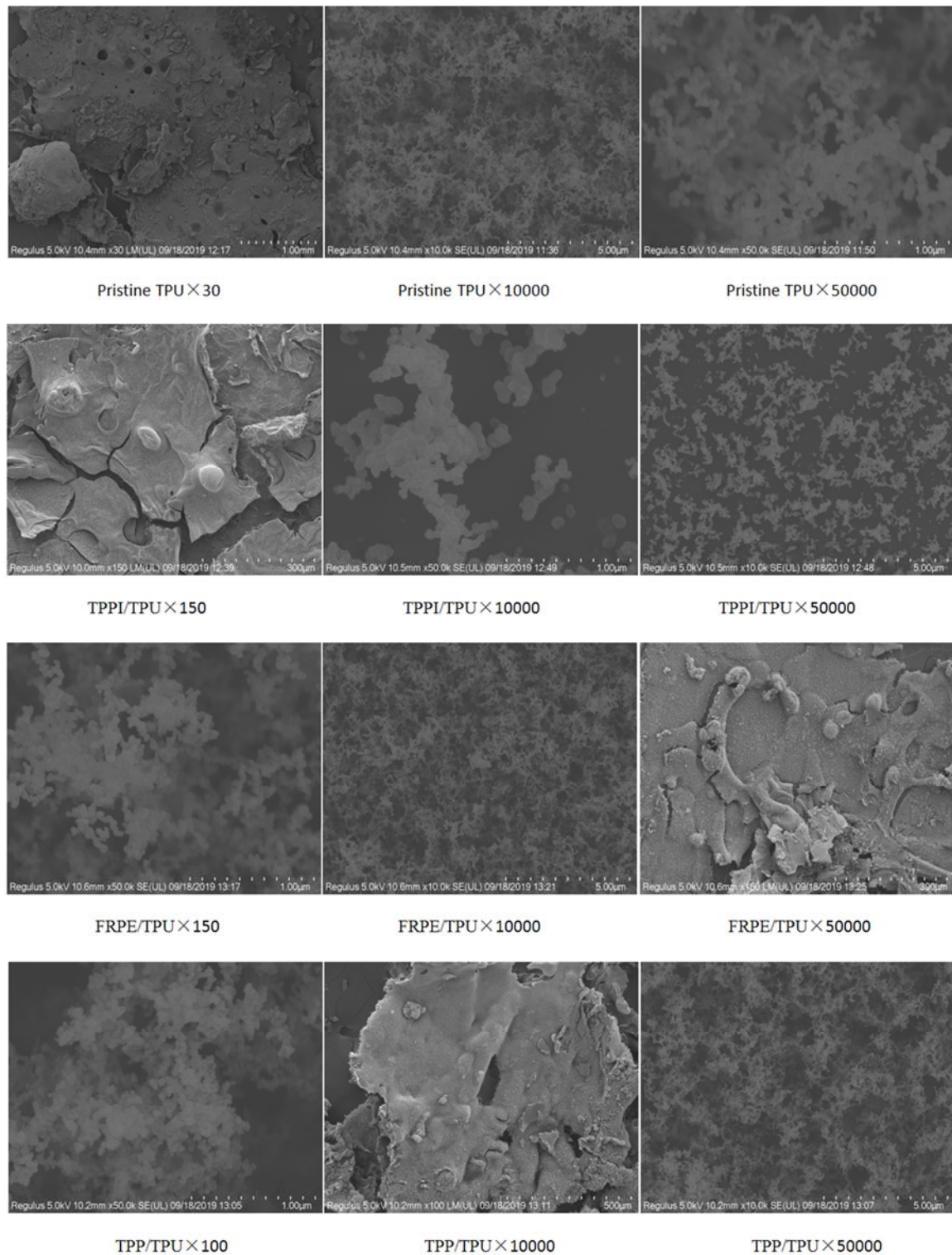**Figure 8.** *Digital photos of fire residues.*

*Figure 9. Micromorphology of fire residues by SEM.*

### 3.4. Residual Chars Analysis of Flame-retardant TPU

The flame-retardant mechanism of flame-retardant TPU are revealed by a systematically study of substances in the vapor phase and the condensed phase during the pyrolysis. The fire behavior in the condensed phase was deduced by FTIR study of flame-retardant TPU's residues after the CC tests (Figure 10). The spectrum of char shows the disappearance of urethane group and the bands at 1587 cm$^{-1}$ was attributed to the stretching viration of aromatic groups and the characteristic absorption peaks of P=O at 1077 cm$^{-1}$ and absorbance of aliphatic hydrocarbons at 2924 cm$^{-1}$ can be observed. This result indicates the formation of phophorus-containing carbonaceous structure. These results show that the phosphate segments in the TPU probably decomposed cross-linked phosphoric acid derivatives, which

could promote the formation of char residues. Therefore, the char acts as an effective thermal insulator to slow down the heat and mass transfer between gas and condensed phases.
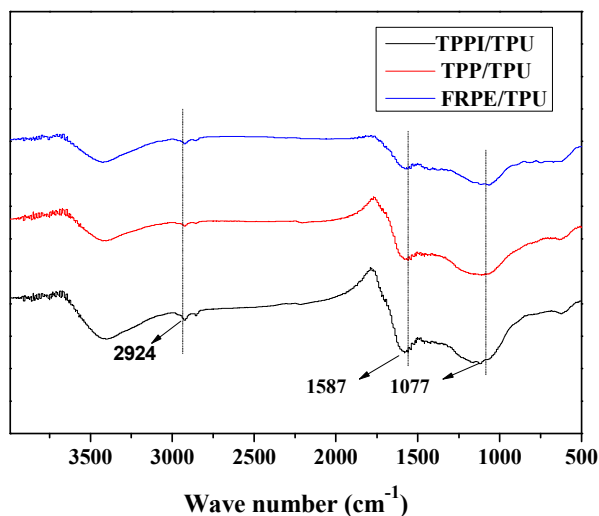


*Figure 10. FTIR spectrum of char residues.*

### 3.5. Thermogravimetric Analysis-infrared Spectrometry

In general, thermogravimetric analysis (TG) coupleed with fourier transform infrared spectroscopy (FTIR) is used to analyze the gaseous products during a thermal degradation process and also probe the degradation mechanism of polymeric materials. All three phosphorus flame retardants were subjected to TG-FTIR analysis under inert condition.

Figure 11 shows the 3D patterns of flame retarded TPU (a, b and c ) filled with phosphorus compounds in different oxidation states. The decomposition products of PU are identified unambiguously by matching the FTIR peaks with standards using the OMNIC software library search and the characteristic strong FTIR signals. The changes in the IR spectra of flame-retardant TPU at different temperatures are displayed in Figure 12. As Figure 12 shows, the main decomposition products for FRPE/TPU in the gas-phase were benzyl acetate (2363 $cm^{-1}$), When the samples were heated to temperatures greater than 350°C, the characteristic absorption peaks of $-CH_2$ and $-CH_3$ were observed (2969 $cm^{-1}$), the band at at 1758 and 1720 $cm^{-1}$ were attributed to the C=O stretching vibration, the peak appear at 1071 $cm^{-1}$ could be assigned to the absorption of O=P-O- vibration in the DOPO, new peaks appear at 1451 and 876 $cm^{-1}$, corresponding to the stretching vibration of the triazine rings, appear above 500°C. When the temperature increases 450°C, the characteristic absorption peaks of P=O (1227 $cm^{-1}$) was observed. In addition. The peak at about 1623 $cm^{-1}$ is due to the stretching vibrations of $NH_3$.

As for TPPI/TPU, The peak at 1080 $cm^{-1}$ could be assigned to the absorptions of the P-O-C vibration in the P-Ph structure. And also observed the peak of hydrocarbons (C-H aliphatic, 2970 $cm^{-1}$). The band at at 1720 and 1363 $cm^{-1}$ were attributed to the C=O stretching vibration. The peak at about 2970 $cm^{-1}$ is due to the stretching vibrations of

$CO_2$. At the peaks 1182 $cm^{-1}$ and 1159 $cm^{-1}$ ascribed to ether. In addition the peaks at 1514 $cm^{-1}$ ascribed to aromatic

As for TPP/TPU, The peak at 3578 $cm^{-1}$ could be assigned to the absorptions of the $H_2O$. And the peak at 2970 $cm^{-1}$ ascribed to the $-CH_3$ and $-CH_2-$. the band at 2280 $cm^{-1}$ was attributed to the vibration absorption –NCO groups, indicating the degradation of the hard segments during the heating process. The band at at 1758 $cm^{-1}$ was attributed to the C=O stretching vibration. The peak at about 2970 $cm^{-1}$ is due to the stretching vibrations of $CO_2$. And the peak at 1201 $cm^{-1}$, 3967 $cm^{-1}$ and 1160 $cm^{-1}$ were ascribed to the P=O, $NH_3$ and the ether, respectively.
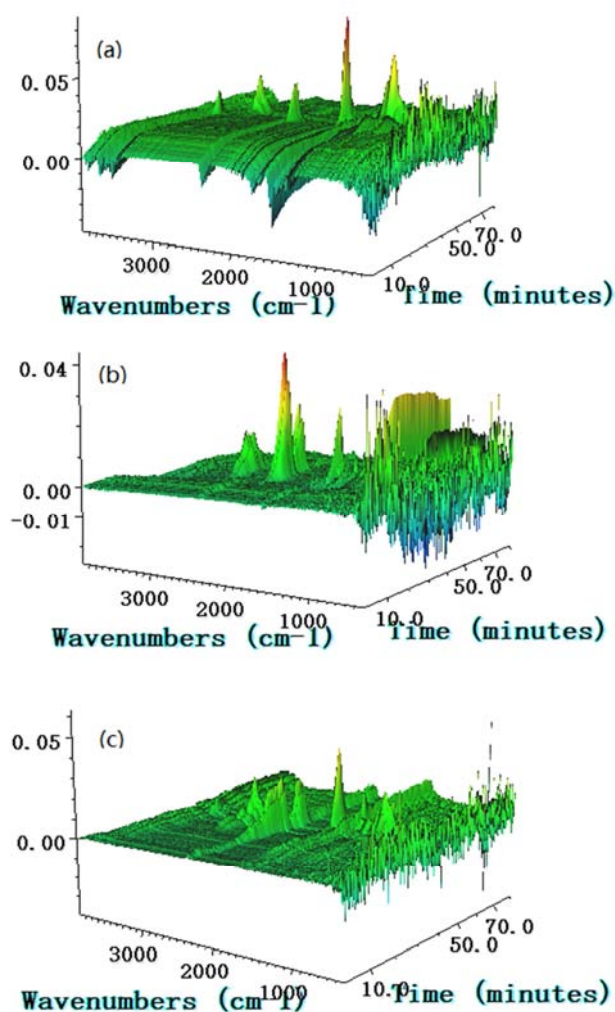


*Figure 11. The 3D TG-IR spectra of gas phase in the thermal decomposition of flame retarded TPUs, (a) FRPE/TPU; (b) TPPI/TPU; (c) TPP/TPU.*

Based on the abovementioned results and analysis, the flame-retardant mechanism of TPPI, TPP and FRPE incorporated TPU are proposed. During the combustion of the TPUs in nitrogen, these phosphorus-containing polyurethane first decomposed to isocyanates and alcohols. With an increase of the temperature, the degradation of phosphorus-containing segments would generate polyphosphoric acids, which promoted the formation of a thermally stable char. Meanwhile, degradation of

phosphorus-containing segments generates incombustible gases, like $H_2O$, $CO_2$, and $NH_3$, which dilute the combustible gas and simultaneously take away some heat. Phosphine and its derivatives evolves into phosphorus-based radicals (e.g. $PO_2\cdot$, $PO\cdot$) in the flame zone, which act as free-radical scavengers to capture the radicals during combustion.
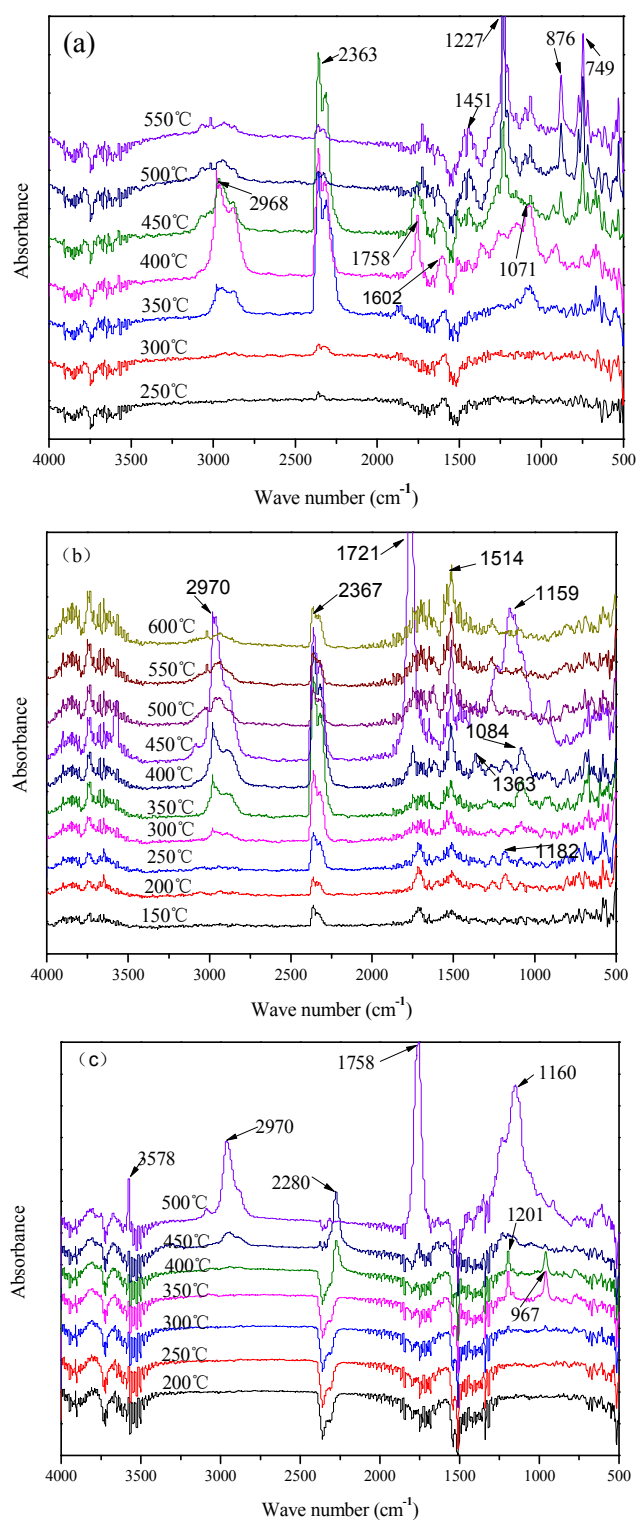


**Figure 12.** *The TG-IR spectra of gas phase in the thermal degradation of pristine and flame retarded TPUs, (a) FRPE/TPU; (b) TPPI/TPU; (c) TPP/TPU.*

# 4. Concliusions

In this paper, a novel reactive type phosphorus and nitrogen-containing polyols was designed and successfully synthesized by one pot polymerization process. The chemical structure of FRPE was confirmed by FTIR. DSC results showed that the melting point of FRPE was 115.6°C. The melting peak is narrow and sharp, so it can be concluded that the synthesized products have high purity. TG and DTG curves show that the maximum weight loss rate temperature is 431.2°C, and the carbon residue rate is 3.5% at 800°C. Accordingly, a series of flame retarded TPU were prepared by additving TPP, TPPI and FRPE with different oxidation state phosphorus, the thermal degradation of pristine and flame retarded TPU were studied by TG and CCT, the results showed that FRPE and TPPI were a kind of good charring agent and that the introduction of it can distinctly enhanced the residues of TPU, furthermore, the carbon residue of FRPE/TPU reached 14.83% at 700°C. DTG and 3D TG-FTIR spectra of gas phase in the thermal decomposition of pristine and flame retarded TPU demonstrated that both FRPE/TPU and pristine TPU were characterized by two main decomposition stages, nevertheless, TPP/TPU and TPPI/TPU were characterized by one and three main decomposition stages, respectively. Based on LOI, TG and CCT, the FRPE/TPU exhibited a significant enhancement in LOI and substantially reduce the PHRR and THR, illustrating an improvement in flame retardancy, it was found that FRPE and TPPI can greatly enhance the thermal stability and promote the char formation of TPU. The exterior residual char after CCT was analyzed by SEM and FTIR, combination with TG-FTIR to identify the degradation mechanism of different oxidation state phosphorus ( +1, +3, +5), all above results indicate that phosphorus in FRPE (+1) and TPPI (+3) play key roles in the condensed phase and could catalyze the formation of char layer compare to pristine TPU. While, phosphorus in TPP (+5) mainly plays a role of flame retardant in the gas phase. FRPE was beneficial to improve the flame retardance of the TPU.

## Acknowledgements

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