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理 學 碩 士 學 位 論 文

Flame Retardant Coating of Polyurethane foam by 4-  
hydroxybenzophenone functionalized polyphosphazene

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## **Abstract**

In this study, the effect of phosphorus-nitrogen flame retardant polymer on the material of the polyurethane foam (PUF) was investigated. 4-hydroxybenzophenone-substituted polyphosphazene was prepared by the ring-opening polymerization of phosphonitrilic chloride trimer at 240 °C, followed by post-modification with sodium 4-benzoylphenyl oxide. Uncoated PUF and coated PUF by resulting polymer were compared and analyzed with TGA and combustion test. The residue contents by thermogravimetric analysis and micrograph by scanning electron microscopy of the resulting polymer were measured to be from 1.75% to 31.7%, showed charred residue by phosphorus-nitrogen flame retardant mechanism, respectively, indicating that the polymer can be used as a good flame retardant coating agent.

## **Keywords.**

Flame retardant, Ring-Opening polymerization, phosphazene, UV-curable



## 1. Introduction

Natural and synthetic polymer materials are used in ever more areas and under ever more demanding environmental conditions. However, fire hazards associated with the use of these polymeric materials, which cause the loss of life and property, are of particular concern among government regulatory bodies, consumers and manufacturers alike.<sup>1</sup> With the increasing trend of more stringent fire safety regulations, demands for reduction of the fire hazard have gained importance in recent years. A suitable flame retardant (FR) treatment might be able to retard the ignition of these materials and/or decrease flame spread, thereby obviating fire hazards and loss of life and destruction of property. Three types of approaches have been quite well accepted and commonly used in various domains. The first common approach involves mechanical incorporation of flame retardant additives into the bulk polymeric matrix, which is mostly low cost and fast blending technique.<sup>2, 3</sup> However, the loading of FR needed to be effective is usually too high, which can lead to a significant influence on the strength and elastic modulus of the materials. The second way to reduce the flammability of the matrix is to bind units chemically to it by using FR segments that contain functional groups. Through this approach the FR element becomes an integral part of the polymer chain and usually results in higher efficiency and longer durability of FR effect. Such incorporation could change the morphology and physical

properties of the bulk polymer, such as melting point, density and glass-transition temperature and presents relatively higher difficulties in industrial manufacturing for certain materials, e.g. fibers, textile and flexible foams, etc.. The third approach which mostly involves surface modification is widely exploited in various commercial applications.<sup>4</sup> The use of fireproof coatings has become one of the most convenient, economical and most efficient way to protect the substrates against fire. Some of its advantages are given as follows: FR coatings allow the concentration of fireproof properties at the surface of the substrate along with preserving the bulk properties of the material (e.g. mechanical properties), and can generally be combined with an attractive aesthetic feature. In most of the cases a fireproof coating represents the only barrier between the fuel and a possible fire source, thus it must withstand effectively throughout the fire, delaying ignition of the substrate, reducing the heat-and-mass transfer between the gas medium and the condensed phase, and hindering propagation of the flame. Based on the flame retarding mechanism, “flame-safe” coatings are classified as either intumescent or non-intumescent types. Intumescent coating can be described as a mixture that has capability to swell and form a three dimensional char layer on top of the substrate when exposed to fire. Traditional intumescent systems consist of a carbon source that acts as a char former (e.g. pentaerythritol), an acid source that acts as a dehydrating catalyst (e.g.

polyphosphate) and a blowing agent that helps form the porous barrier (e.g. melamine, guanidine). This carbonaceous cellular/porous-like residue acts as a barrier to heat, air and pyrolysis products, and finally shields the underlying substrate from fire spread.<sup>5</sup>

In this study, We use polyphosphazene, which have synergism about flame retardancy of phosphorus and nitrogen.<sup>6-8</sup> Beside, Chlorine of poly(dichlorophosphzene) was substituted by 4-hydroxybenzophenone via post-modification because of curablility by UV. The synthesized P1 by the above method prepared as 1, 2 wt% P1 solution and coated Pure-PUF to confirm thermal stability and char residue.

## 2. Experimental

**Materials.** All reactions were carried out under an atmosphere of dry argon using standard Schlenk line techniques. Tetrahydrofuran (THF) was obtained from Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Phosphonitrilic chloride (Haihang Industry, Jinan, Co., Ltd.), Sulfamic acid (Aldrich, 99%), NaH (Aldrich, dry, 95%), 1,2,4-trichlorobenzene (DAEJUNG), Calcium Sulfate dihydrate (DAEJUNG, 97%), 4-Hydroxybenzophenone (Alfa, 98%) and Dichloromethane (DCM, sk chmical) were purchased and used directly. In case of synthesis of polyurethane foam, multifunctional polyol (NP-360), multifunctional isocyanate (S-5005), silicon surfactant (B-8462) and catalysis (T-33LV) were used without purification as delivered from PYURAN co., Ltd. Deionized water was used as natural blowing agent.

**Characterization.**  $^3\text{H}$  NMR spectra were collected in  $\text{CDCl}_3$  on a Bruker avance 300 MHz NMR spectrometer. Scanning electron microscopy (SEM) was carried out in a JSM-7610F (JEOL Ltd.) EDS analysis of the residual char layer of the burned P1, Pure-PUF and 2 wt% PPZ-PUF were done by Oxford Xmax50 Energy dispersive spectroscopy. Thermogravimetric analysis (TGA) of the Pure-PUF and flame retardant PPZ-PUF was performed using a Q-50 (TA) instrument. About 10.0 mg of sample was put in a platinum plate and heated from 25 to 600 °C. The heating rate was set as 10 °C/min (nitrogen atmosphere, flow rate of 60 ml/min).

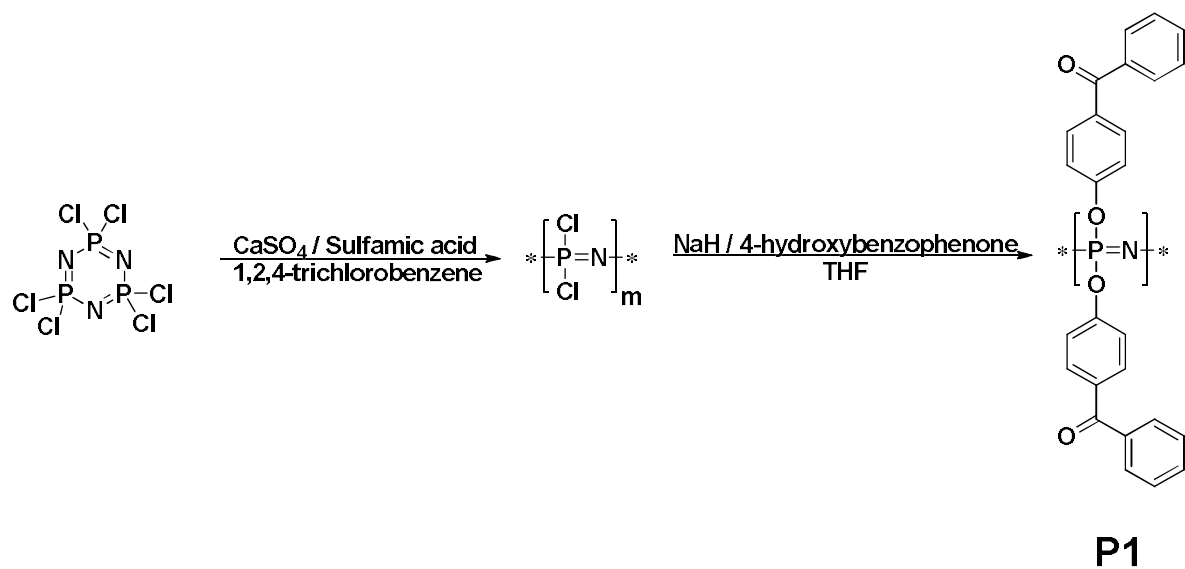
## Synthesis.

**Poly(bis(4-benzoylphenyl)phosphazene) (P1).** The synthesis procedure is illustrated in Scheme 1.<sup>9-16</sup> The phosphonitrilic chloride (20g) with 1, 2, 4-trichlorobenzene (16 mL) was placed in a 50-mL two-neck round-bottom flask. The catalyst, sulfamic acid (85.28 mg), and the promoter,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (75.76mg) were also added to the flask. The reaction mixture was stirred and constantly heated to maintain its temperature at 210 °C. Dry nitrogen was bubbled through the reaction mixture. As the reaction progressed, the reaction mixture became viscous and it was stopped before cross-linking occurred. The yield was approximately 35% under these conditions. It took an hour for the reaction mixture to become viscous in the presence of the promoter. The polymer was precipitated by pouring into 400 mL of hexane. The unreacted trimer dissolved in hexane and separated from the polymer. Poly(dichlorophosphazene) was then dissolved in 150 mL of tetrahydrofuran. Crosslinked polymer, if present, does not dissolve in this solvent and may be removed by filtration.

Poly(dichlorophosphazene) (1.16 g, 10mmol) was dissolved in THF (100 mL) in a 500 mL Schlenk flask (the main reactor). 4-hydroxy benzophenone (5.94 g, 30 mmol) was added dropwise to a THF suspension (150 mL) of NaH (0.79g, 33 mmol) in a second Schlenk flask, and the mixture was stirred for 0.5 h until it became a clear solution. This

solution was then added slowly to the main Schlenk flask, and the mixture was stirred for 8 h at 25 °C. After 8 h at 25°C reaction was terminated. The suspension was concentrated by evaporation and was poured into water sequentially three times.

### 3. Results and Discussion

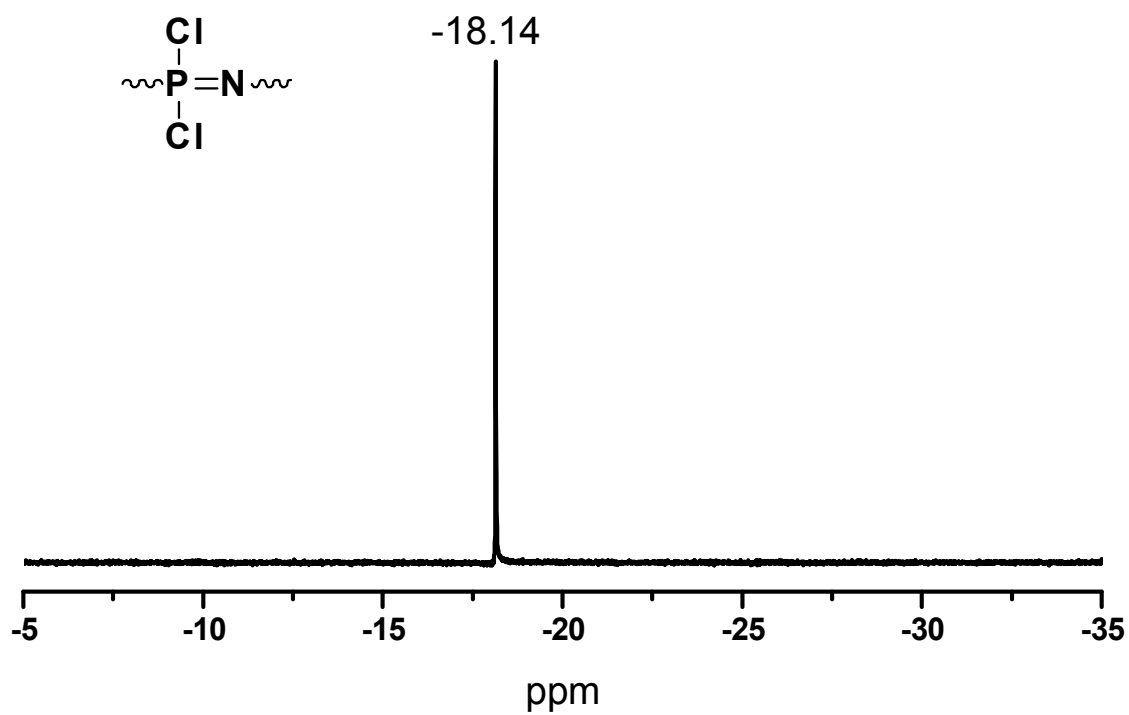


**Scheme 1** Synthesis of UV curable flame retardant polymer by ring-opening polymerization and post-modification

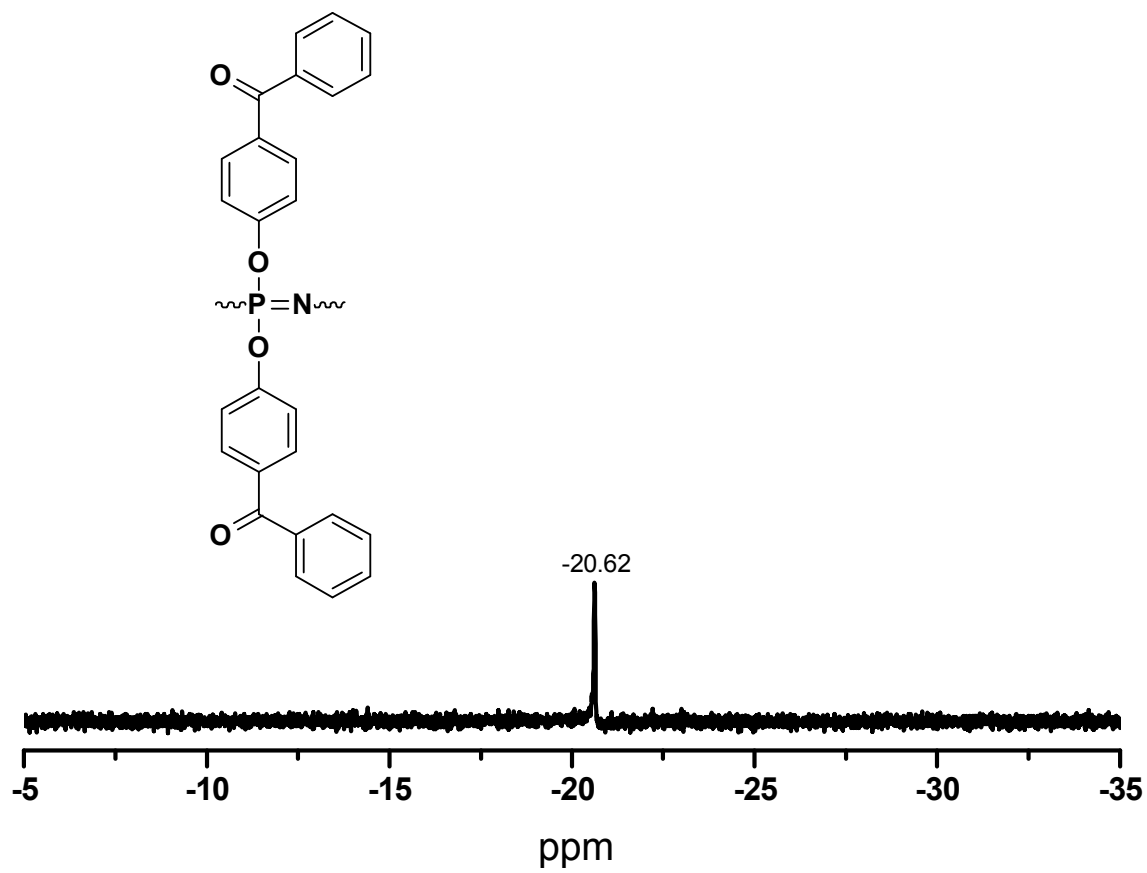


### 3.1 Synthesis of Poly(bis(4-benzoylphenyl)phosphazene) (P1)

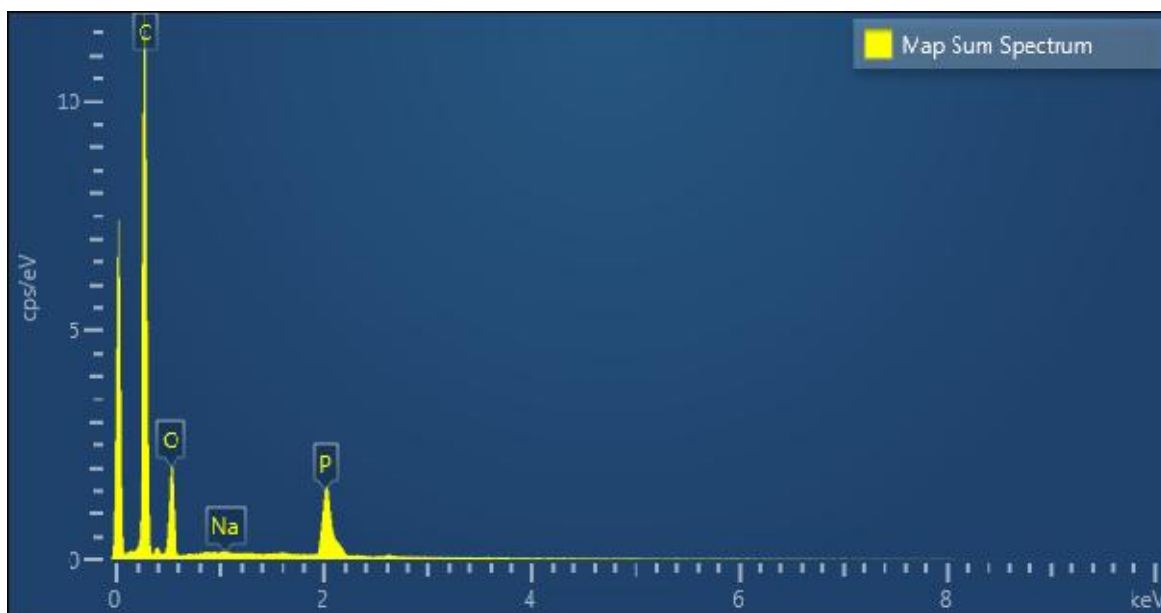
P1 was successfully synthesized by ring-opening polymerization of cyclic hexachlorotriphosphazene and subsequent nucleophilic substitution of the chlorine atoms by 4-benzoylphenolate as shown in Scheme 1. The material is well soluble in chloroform. The  $^{31}\text{P}$  NMR spectrum exhibits one singlet at  $-18.14$  ppm (Fig. 1), which indicates the presence of a non-crosslinked polymer with a typical chemical shift for a polyphosphazene.<sup>17-19</sup> Post-modification proceeded, The one sharp  $^{31}\text{P}$  NMR peak of P1 shifted to  $-20.62$  (Fig 2). In addition, the SEM-EDS data exhibits the composition ratio for a P1. As shown Fig. 1, the composition ratio of the atom of P1 is 1 P, 4 O and 24 C, which were confirmed to be in agreement with the data of SEM-EDS.



**Figure 1.**  $^{31}\text{P}$  NMR spectrum of poly(dichlorophosphazene)



**Figure 2.**  $^{31}\text{P}$  NMR spectrum of P1



Element	C	O	Na	P	Total
<b>Wt (%)</b>	<b>73.8</b>	<b>19</b>	<b>0</b>	<b>7.2</b>	<b>100</b>
<b>Composition (%)</b>	<b>81.2</b>	<b>15.7</b>	<b>0</b>	<b>3.11</b>	<b>100</b>

**Figure 3.** SEM-EDS data of P1

### 3.2 Thermal stability

Its thermal stability is very important when a polymeric material is used as a flame retardant, which mainly concerns the release of decomposition products and the formation of a char.<sup>20, 21</sup> Fig. 4 and 5 show the TGA and derivative thermogravimetric analysis (DTG) curves of Pure-PUF, P1, 1 wt% PPZ-PUF and 2 wt% PPZ-PUF. Pure-PUF has one main decomposition processes. It begins to decompose at about 300 °C (5.0 wt% weight loss). Continuously, the process occurs above 300°C, which is the main decomposition process of Pure-PUF. The temperatures of maximum mass loss rate (T max) for the one step is 348.58°C as is shown in Figure 5. The residue of Pure-PUF at 600 °C is only about 1.75 wt%. For 1 wt% PPZ-PUF and 2 wt% PPZ-PUF, their initial decomposition temperatures are 275 and 260 °C, respectively. They are lower than that of Pure-PUF. In the first process, 1 wt% PPZ-PUF and 2 wt% PPZ-PUF decompose faster than Pure-PUF owing to the less thermal stability of phosphorus-nitrogen in flame retardant composites. The reduction of initial decomposition temperature is attributed to the fact that P O C is less stable than common C C bond. The degraded phosphate group makes a big contribution to the formation of the compact char residue, which protects the sample from further degradation. Beyond the temperature of 350 °C, 1 wt% PPZ-PUF and 2 wt% PPZ-PUF are more stable than Pure-PUF. From figure 4 and 5. The residue of Pure-PUF and 2

wt% PPZ-PUF at 600°C are 1.75% and 37.46%, respectively.

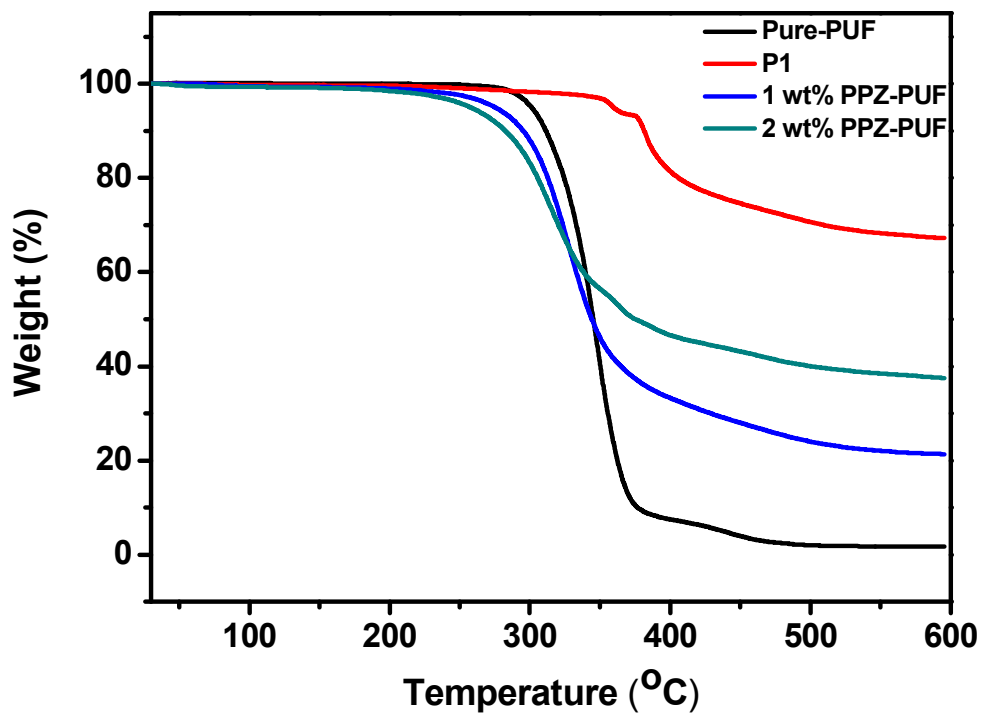
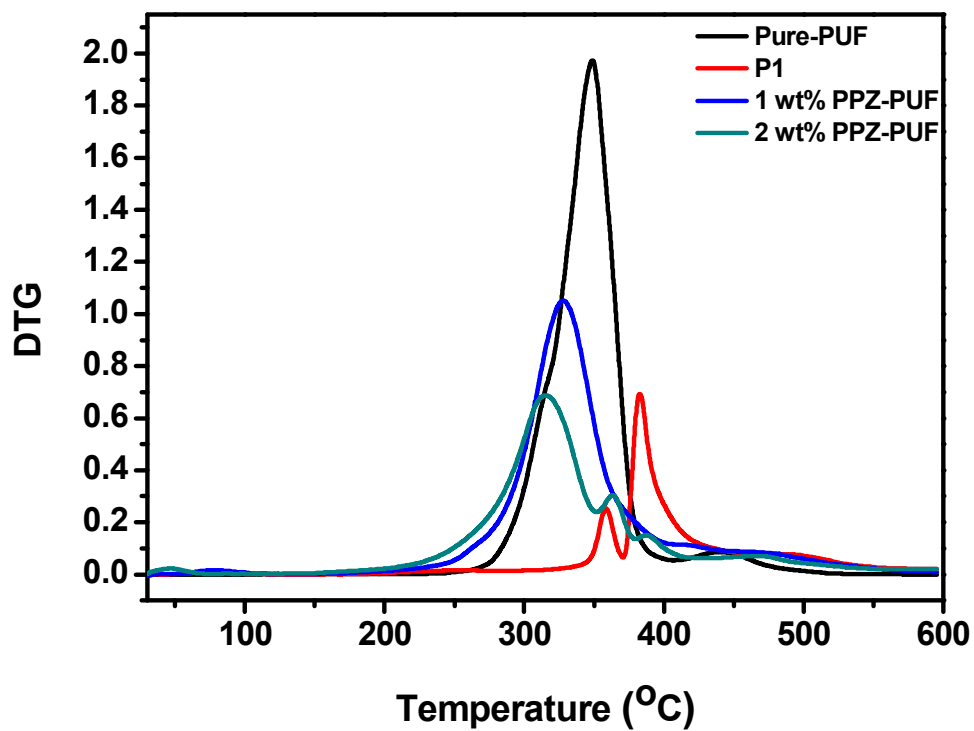


Figure 4. TGA results of Pure-PUF, P1, 1 wt% PPZ-PUF and 2 wt% PPZ-PUF

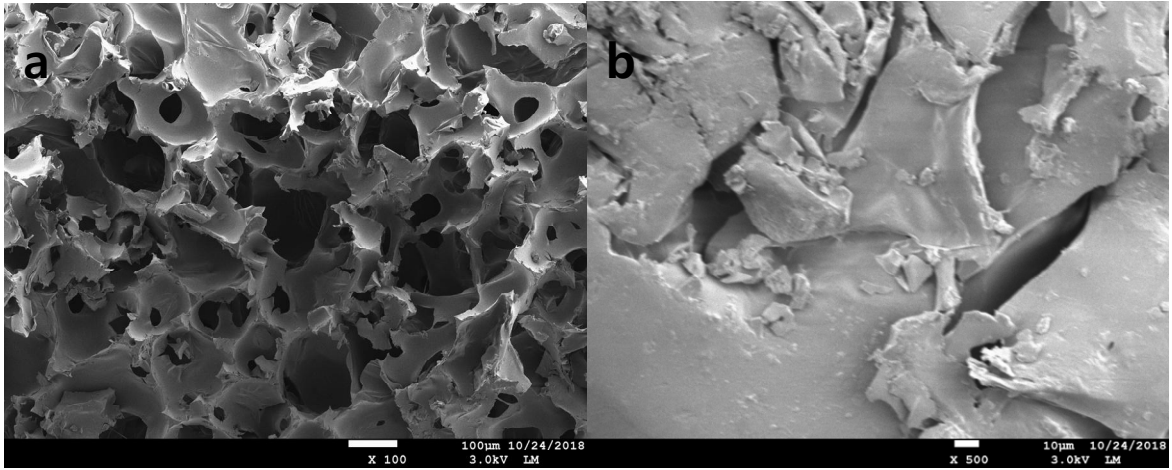


**Figure 5.** DTG results of Pure-PUF, P1, 1wt% PPZ-PUF and 2 wt% PPZ-PUF



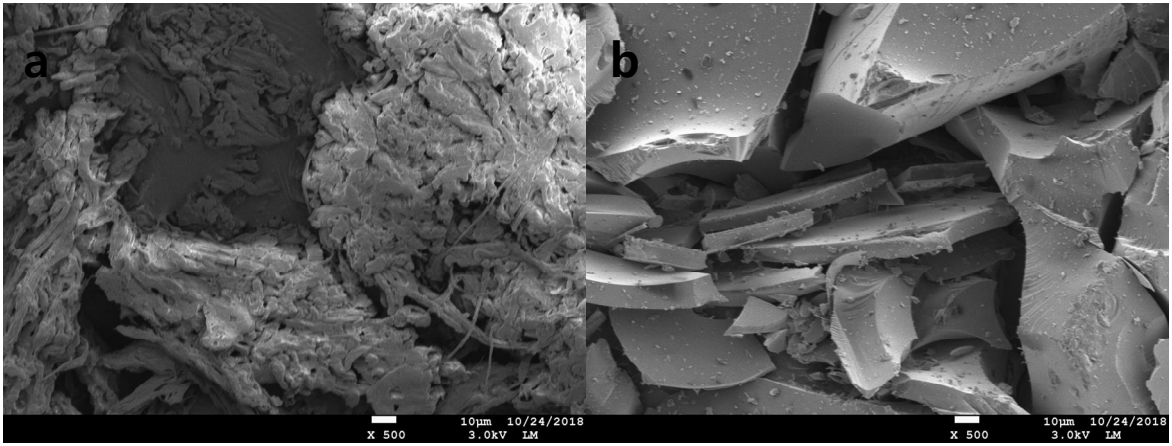
### **3.3 Morphologic structure of the charred crusts**

Pure-PUF, P1 and 1, 2 wt% PPZ-PUF composites were burnt in air respectively and their residue was collected for the test. The micrographs by scanning electron microscopy of the char residue and original structure of Pure-PUF were shown in Fig. 6a and 6b. It was found that the Pure-PUF char residue appeared soft. It looked like a clay-like structure formed by melting in the process of burning. An intumescent flame retardant mechanism for P1 was proposed which based on the gaseous decomposition and the solid decomposition products during pyrolysis and the residual char after burning.<sup>22-24</sup>



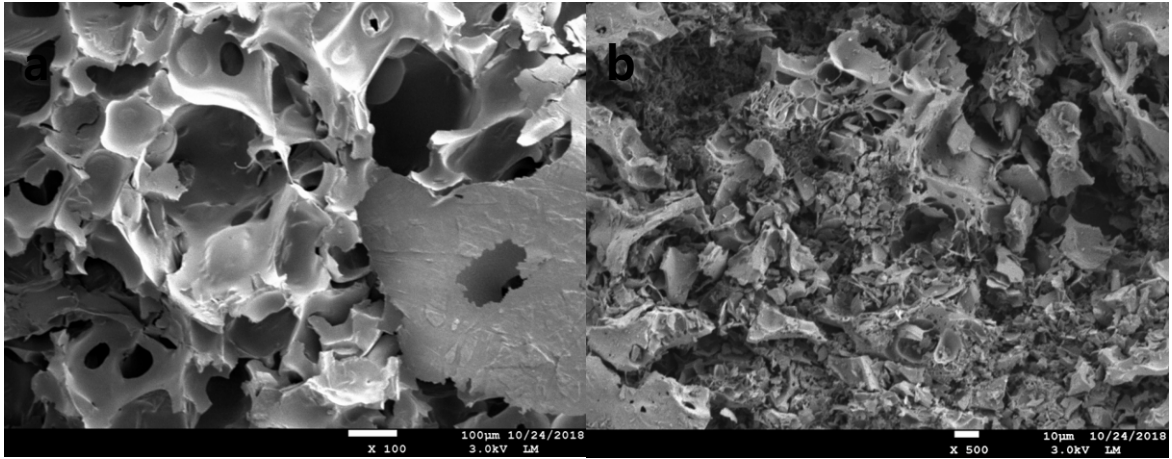
**Figure 6.** SEM micrograph of Pure-PUF (a) and char residue of Pure-PUF (b).

Fig. 7 show the morphology of the P1 and char residue of P1. As shown in Fig 7a, there appeared soft face, but in case of P1 was burnt in Fig 7b, the form of residue appeared hard and compact. A compact char layer acts as a barrier and can help to protect the fiber against heat and flames. The morphology and composition of the formed char affects the flame retardant mechanism.



**Figure 7.** SEM micrograph of P1 (a) and char residue of P1 (b).

Fig. 8 showed the morphology of the char residue of treated and untreated P1. As shown in Fig. 8a and b, there were many big and small holes on the outer and inner surfaces of PUF. In the case of the coated PPZ-PUF, the outer of residue appeared compact but the inner remained porous. As discussed above, char layer were formed because of formation of polymetaphosphoric acid during combustion. The char structure with a continuous outer surface, polymetaphosphoric acid and nitrogen could make the gaseous decomposition products and provide a good barrier to heat and mass transfer in burning. Thus both thermal behaviours and flammability properties were improved.

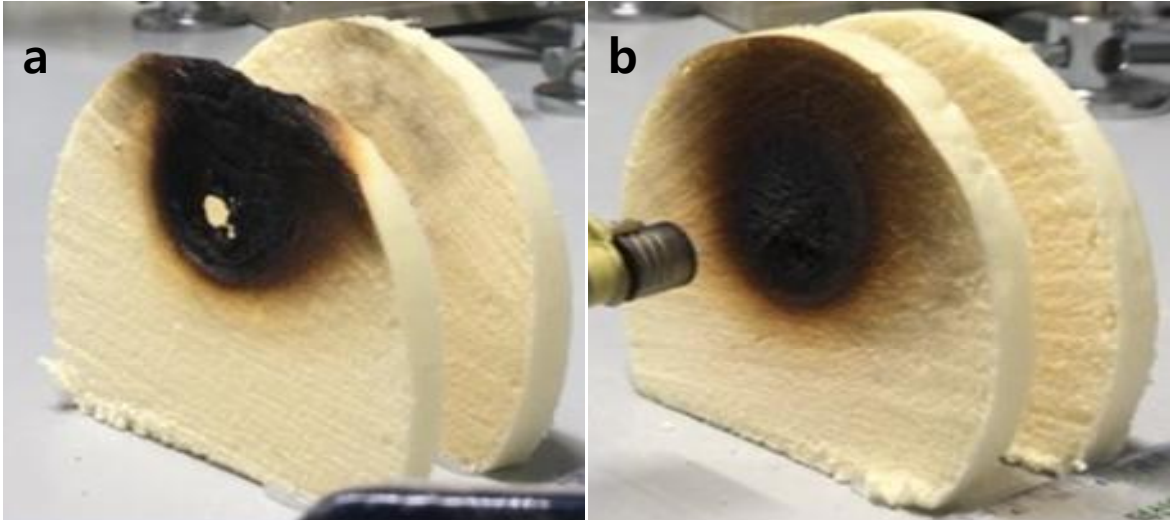


**Figure 8.** SEM micrograph of 2 wt% PPZ-PUF (a) and char residue of 2 wt% PPZ-PUF

(b)

### **3.4 Flame-retardant Properties**

The fire-resistant behavior of Pure-PPZ and PPZ-PUF were analyzed through the simple measurement of the char yield. Figure 8 shows the pictures of combustion test samples of Pure-PUF (a) and PPZ-PUF (b). It clearly indicates that the PPZ-PUF samples had more solid carbon-rich char on the burnt surface than the Pure-PUF. This was mainly because of the reaction of P1 which generated gases at high temperatures and polymetaphosphoric acid for blocking char layer. This char prevented the PPZ-PUF from burning further.



**Figure 9.** Photographs of combustion test samples of Pure-PPZ(a) and PPZ-PUF(b).



#### 4. Conclusions

PUF was synthesized by conventional method. Substitution reaction using poly(dichlorophosphazene) via ring-opening polymerization were performed. The chemical structure and reaction mechanism are elucidated. PUFs were coated with 1, 2 wt% P1 solution and it exhibited improved flame retardancy and thermal stability. The TGA results indicated that the coating of P1 onto PUF dramatically improves the char yields and the thermal stability of the char at high temperatures due to synergistic effect of the presence of nitrogen and phosphorus in backbone of P1. In conclusion, During combustion, the P–O–C bonds break fast, and form P–O–P structure in the residual char, which has a positive effect to form an expanding and compact charred crust to protect the underlying polymeric material from further attack from flame or heating. And nitrogen also made inert gas, which diluted surrounding oxygen concentration.

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## 국문 요약

폴리우레탄 (TPU)은 개발이래로 현재까지 다양한 산업 분야와 범위에서 적용되고 사용되고 있다. 이러한 사용 범위의 확대와 사용량의 증가는 더불어 폴리우레탄이 열에 취약하다는 점을 부각해왔다. 이러한 열에 의한 취약점을 보완하고자 난연제의 사용을 야기했다. 그러나 다양한 난연제의 등장과 함께 TPU의 물성 저하의 문제 및 친환경적 문제가 지속적으로 발생하고 있다. 본 연구에서는 인이 포함된 난연 고분자를 합성하여 폴리우레탄 소재에 UV를 이용한 친환경적 코팅 후 난연 성능이 부여되는지 확인하였다. 인과 질소로 이루어진 모노머인 phosphonitrilic chloride를 개환 중합하여 poly(dichlorophosphazene)을 얻은 후 sodium 4-benzoylphenyl oxide를 천천히 가하여 UV가교성이 있는 치환기를 가지는 poly(bis(4-benzoylphenyl)phosphazene) (Benzo-PPZ)을 합성하였다. 얻어진 고분자를 이용해 코팅한 폴리우레탄 폼 (PPZ-PUF)와 코팅하지 않은 폴리우레탄 폼 (pure-PUF)을 비교 분석하였다. TGA분석을 통해 P1 코팅 후 PUF의 잔여물 무게비가 30.9%증가했으며, SEM을 통해 PPZ-PUF의 연소 후 표면에서 인계 난연 메커니즘에 의한 탄소 피막 보호층을 관찰할 수 있었다. 연소시험의 digital image를 통해 PPZ-PUF가 pure-PUF에 우수한 난연 효과와 열 차단효과를 부여하는 것을 확인하였다.