

# 透氣型功能性樹脂之合成與應用之探討-子計畫二： 功能性水性 PU 磷氮架橋劑之阻燃及架橋性質探討

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## 中文摘要

合成之含磷架橋劑可同時當作水性 PU 樹脂之架橋劑和阻燃劑。此種後架橋之水性 PU 樹脂的物理和機械性質隨著架橋劑的用量而改變。至於此後架橋之水性 PU 樹脂的熱安定性和阻燃性質則分別利用熱重分析儀，動態機械熱分儀，限氧指數和錐形熱卡儀等儀器評估。

## Abstract

The phosphorus-containing curing agents were prepared and served as the post-curing agent and as the flame retardant for aqueous-based PU, simultaneously. The physical and the mechanical properties of resulted PU were modified corresponding to the curing dosage. Whereas the thermal stability and the flame inhibition behaviors of these post-cured PU were evaluated by the measurements of thermogravimetric analysis, dynamic mechanical thermal analysis, limiting oxygen index and cone calorimeter, respectively.

*Key Words:* aqueous-based PU, thermal stability, flame inhibition, cross-linking

## 二、計畫緣由與目的

Anionic aqueous-based polyurethane (PU) was prepared by a conventional method<sup>1</sup>. The hydrophilic carboxyl group stabilized the aqueous PU dispersion and also served as PU reactive site toward a post-curing agent<sup>1-3</sup>. The properties of these aqueous-based PU were modified by various curing reactions<sup>4,5</sup>.

Phosphorus-containing compound functioned as the flame retardant for the polymeric materials<sup>6-11</sup>. Furthermore, the flame retardant consisted of both phosphorus and nitrogen compositions performed the synergistic effect on flame inhibition<sup>7</sup>. It was due to this phosphorus-oxygen (P-O) bond strength was significantly lower than those of C-O bond on PU main chain<sup>12,13</sup>.

The reactive flame retardant consisted of phosphorus and nitrogen composition was prepared from the substitution reactions of phosphorus oxychloride and phenylphosphonic dichloride by aziridine, respectively. The aziridinyl group on these prepared flame

retardants was reactive toward PU carboxyl group and resulted the chemically bonded phosphorus amino ester linkages formation between polymer main chains<sup>13</sup>. By means of this type curing reaction and the resulted polymer had the better thermal stability and flame inhibition behaviors than original PU.

## 三、研究方法及成果

### Materials

Triethylamine (TEA), phosphorus oxychloride (POCl<sub>3</sub>), phenylphosphonic dichloride, phenol and 2,2-Dimethylolpropanoic acid (DMPA) were obtained from Aldrich Chemical Co. These materials were distilled or recrystallized before using for other preparation. Isophorone diisocyanate (IPDI) and polypropylene glycol-2000 (PPG-2000) were supplied by Huls and Arco Chemical Co., respectively. They were used as received without further purification.

### Preparation of Anionic Aqueous-Based PU dispersions<sup>1</sup>

PPG-2000 (0.1 mol) and DMPA (0.1 mol) were dried at 110°C overnight before mixing with IPDI (0.3 mole) in a 500-mL 4-necked resin flask. The reaction was carried out and kept at 90°C for 4 hrs until the percentage of NCO dropped below 3.0%. The freshly dried acetone was then added into the flask to adjust the viscosity of PU prepolymer. The PU dispersion was then prepared by mixing these PU prepolymers with the aqueous solution of TEA (0.1 mol) at a high shear rate. The prepared PU dispersion consisted of 30% solid contents and its pH value was about 8.0 after acetone was removed from this aqueous dispersion.

### Preparation of Aziridinophenyl Phosphonate (PDA)

A 200 mL dried toluene solution of 0.3 moles phenylphosphonic dichloride was put into a 500 mL 3-necked flask and which was kept in an ice bath and equipped with a calcium chloride drying tube. A 100 mL toluene solution with 0.6 moles of freshly distilled aziridine and triethylamine was added through an additional funnel. The reaction mixture was kept constant agitation in an ice bath under nitrogen for 3 hours and then overnight at

ambient temperature. The white triethylamine hydrochloride salt was first filtered out from the reacted mixture after the reaction. The residue was then collected after toluene was distilled off from the filtrate. The residue was separated by using a silica gel column and eluted with chloroform, and the final product PDA was isolated with 60% yield (Scheme I).

### Preparation of Phenyl Diaziridinyl Phosphoramidate (PHA)<sup>12</sup>

A 200 mL toluene solution with 0.3 moles of phosphorus oxychloride ( $\text{POCl}_3$ ) was in a 3-necked flask which was kept in an ice bath and equipped with a calcium chloride drying tube. A 100 mL solution of toluene with 0.3 moles of freshly dried phenol and triethylamine was then added into the reaction flask through an addition funnel. The reaction mixture was agitated at  $0^\circ\text{C}$  for 3 hours under nitrogen atmosphere and then maintained at ambient temperature for 24 hours. A 100 mL solution of toluene with 0.6 moles of aziridine and triethylamine was added and agitated for overnight. After reaction, white triethylamine hydrochloride salts were removed from the reaction mixture by filtration. Yellow precipitates were collected after the toluene was distilled off from the filtrate under vacuum. The reaction yield was 40% for PHA (Scheme II).

### Aqueous-based PU with Reactive Phosphorus Flame Retardant

The aqueous-based PU dispersion was treated with the prepared flame retardant, PDA and PHA, respectively. The curing reaction took place between the aziridinyl group of flame retardant and PU carboxyl group on film drying. The performance properties of post-cured PU were summarized in Table I. Detailed experimental procedures for the determination of PU properties were described in the following sections.

### Tensile and Physical Properties of Post-cured PU Films

PU films were cast and air-dried from these prepared PU dispersions at ambient temperature and then dried at  $50^\circ\text{C}$  for 24 hours. These dried PU films were conditioned in a 75% relative humidity chamber at  $25^\circ\text{C}$  for 72 hours before the measurements. The tensile experiments were performed on Shimadzu Universal Testing Machine model Autograph S-100-C. Dumbbell shape specimens with 1.0mm thickness were used to determine the tensile properties of the post-cured PU films. The test was performed at a cross-head speed of 40 mm/min. and a gauge length of 40mm. Six tests of each PU sample were taken, and the three measurements that showed the highest tensile strength for calculating the mean value were selected (Table I).

### Gel Content

A known weight of dried PU film was put into a Soxhlet extractor and extracted continuously with tetrahydrofuran for 24 hours. The gel remained after extraction was dried and calculated according to the test results. Gel content of the cured PU films were shown in Table I.

### Ethanol Swollen

A known weight ( $W_0$ ) of dried PU film with a dimension of 60 x 60 x 1 mm was immersed in ethanol (95%) bath for 48 hours. The towel-wiped dry sample weights ( $W_1$ ) and oven-dried PU film weight ( $W_2$ ) were obtained. Ethanol absorption ( $W_e$ ) and the weight loss ( $W_y\%$ ) of PU film in ethanol were calculated according to the following equations, respectively.

$$W_e\% = \frac{W_1 - W_2}{W_2} \times 100\%$$

where  $W_e$  is the amount of ethanol absorption by PU film

$$W_y\% = \frac{W_0 - W_2}{W_0} \times 100\%$$

where  $W_y$  is the amount of PU dissolved in ethanol

### Dynamic Mechanical Thermal Behaviors

The PU films were dried at  $50^\circ\text{C}$  for 24 hours and conditioned in a 75% relative humidity chamber at  $25^\circ\text{C}$  for 72 hours before test. Dynamic mechanical thermal analysis (DMTA) measurements of PU films were performed on a Polymer Laboratories DMTA instrument model MK-II. All data were measured in bending mode at temperature ranging from  $-80$  to  $150^\circ\text{C}$ , with 1.0 Hz frequency and a heating rate of  $3^\circ\text{C}/\text{min}$ .

### Thermogravimetric Analysis

Each PU sample ( $\sim 10$  mg) was measured by a thermogravimetric analyzer model Hi-Resolution 2950 with a heating rate of  $10^\circ\text{C}/\text{min}$ . from ambient temperature to  $500^\circ\text{C}$  under air and nitrogen atmosphere, respectively.

### Limiting Oxygen Index

The limiting oxygen index (L.O.I.) values of polymer films were measured with a Fire Testing Laboratories instrument. The specimen dimension was 150 x 500 x 1.2 mm. The L.O.I. value was determined as suggested by ASTM D 2863-74 and calculated according to the following equation.

$$\text{L. O. I.} = \frac{[\text{O}_2]}{[\text{N}_2] + [\text{O}_2]} \times 100\%$$

where  $[\text{N}_2]$  and  $[\text{O}_2]$  are the concentration of nitrogen and oxygen in a mixture of nitrogen and oxygen, respectively.

#### Cone Calorimeter Measurement

The combustion measurements were carried out according to ISO 5660 on a Cone Calorimeter from Fire Testing Laboratories Ltd. The specimen dimension was 100 x 100 x 1.2 mm. Triplicate tests were performed for the measurement of the heat release rate and a time to ignition at a heat flux of 20 kW/m<sup>2</sup>.

#### 四、結果與討論

The polymer contained both phosphorus and nitrogen contents and demonstrated the synergistic effect on flame inhibition properties<sup>6,7</sup>. It was due to the formation of a condensed phase and a non-flammable gas phase from their phosphorus and nitrogen compositions and blocked the air supply to polymer surface and promoted the char formation at high temperature<sup>14</sup>.

Two types flame retardants were prepared from the substitutions of phosphorus oxychloride and phenylphosphonic dichloride with aziridine, respectively (Schemes I and II) The composition of PDA consisted of 14.90 and 13.46% phosphorus and nitrogen contents, whereas PHA consisted of 13.84 and 12.50% phosphorus and nitrogen contents, respectively (Table II).

#### Physical and Mechanical Properties

Their gel contents were increased from nil to 80.1-85.8% and 67.6-88.3% after aqueous-based PU cured with 1.4 and 11.4 phr PDA and PHA, respectively. The original PU dissolved into ethanol (95%,v/v) completely at ambient temperature. However, PU curing system with PDA and PHA (PDA-PU and PHA-PU) had ethanol swollen of 3356-670% and 2197-724%, respectively (Table I). The results demonstrated PHA-PU had the better polymeric network formation than those of PDA-PU system.

The tensile strength at break of the original aqueous-based PU system is 3.5 kg/cm<sup>2</sup> at 725% elongation, and it becomes to 5.8 kg/cm<sup>2</sup> at 677% and 6.6 kg/cm<sup>2</sup> at 560% elongation after it is cured with 1.4 phr PDA and PHA, respectively (Table I). It is due to the steric hindrance of polymeric structure or the excess dosage of PDA or PHA, its aziridinyl group has no chance to react with PU carboxyl group in polymer matrix, the un-reacted post-curing agent serves as a plasticizer in the

final polymer.

#### Thermal Behaviors

The thermal oxidative stability of aqueous-based PU is improved after it is treated with various dosages of PDA or PHA (Table III). Due to the cross-linking reaction takes place between this phosphorus and aziridinyl curing agent, and additional 0.07 - 0.55% phosphorus and 0.06-0.54% nitrogen from this post-curing agent also plays an important role to boost the thermal oxidative stability and the char yield of final PU.

Dynamic mechanical thermal analysis (DMTA) data also confirms the curing behaviors of PDA and PHA on this aqueous-based PU curing system. The intensity of tan  $\delta$  peak (at -40°C) on PU soft segment decreases as the dosage of PDA or PHA curing agent increases from 2.9 to 11.4 phr, it exhibits the decreases on polymer free volume as well as the degree of freedom.

#### Flammability

The original aqueous-based PU has L.O.I. value 20, and the L.O.I. value increases to 25.0 and 25.2 after PU is cured with 2.9 and 11.4 phr PHA, respectively (Table I). Both PU curing systems have 0.14 and 0.55% phosphorus and 0.13 and 0.50% additional nitrogen contents on the final cured PU, respectively (Table II). Whereas the PU curing system with 2.9 phr PDA, it consists of 0.15 % phosphorus and 0.13 % additional nitrogen, and its L.O.I. value is 26.2. These phenomena confirmed the synergistic flame retardation mechanism on PU curing system by these phosphorus flame retardants.

The ignition time of original PU is 49 seconds at a heat flux of 20 kW/m<sup>2</sup> and the cured PU is 81, 90, 118 and 122 seconds with 1.4, 2.9, 7.1 and 11.4 phr PDA, respectively. The average heat of combustion on the cured PU decreases to 21-25 from 29 MJ/kg of the original PU after it is treated with PHA or PDA (1.4 to 11.4 phr dosages). PHA-PU or PDA-PU post-curing system has longer ignition time and lower average heat of combustion than original PU.

#### 五、結論

PU cured system with these reactive phosphorus flame retardant, PDA-PU or PHA-PU exhibits better thermal stability, flame inhibition, physical and mechanical properties than those of original PU. Either PHA or PDA serves as the reactive flame retardant and the post-curing agent for aqueous-based PU, simultaneously. Char yield, thermal stability, mechanical and physical properties of PHA-PU are higher than PDA-PU, these are due to the cross-linking density of PHA-PU is higher than the other system. The ignition time and the average heat of combustion of PHA-

PU and PDA-PU are similar and both are better than those of the original PU. These results are confirmed by the contribution of phosphorus and additional nitrogen contents from these reactive phosphorus flame retardants, respectively.

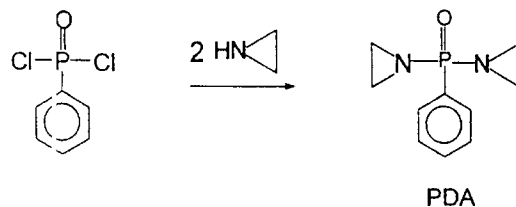
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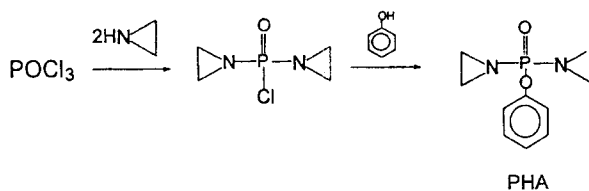
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## Scheme I Preparation of PDA



## Scheme II Preparation of PHA



## Scheme III Curing Reaction of Aqueous-Based PU with PDA or PHA

