



# Coated vs. naked red phosphorus: A comparative study on their fire retardancy and smoke suppression for rigid polyurethane foams



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## ARTICLE INFO

### Article history:

Received 10 August 2016  
Received in revised form  
1 December 2016  
Accepted 11 December 2016  
Available online 22 December 2016

### Keywords:

Red phosphorus  
Coating  
Polyurethane foam  
Smoke suppression  
Flame retardancy

## ABSTRACT

Red phosphorus (RP) and the coated RP with melamine formaldehyde resin (MFcP) were foamed with isocyanates to prepare polyurethane foam (PUF). The cell size of PUF/RP became uneven and more spherical, and the cell struts became thicker. The cells of PUF/MFcP were much more uniform in size and more spherical in shape. Addition of flame retardants increased the densities, compressive strength and thermal conductivity of the foams, but decreased the blind hole percents. Thermal gravimetric analysis (TGA) tests exhibited that decomposition of both PUF/RP and PUF/MFcP took place at lower temperatures than that of neat PUF. However, the maximum decomposition temperature ( $T_{max}$ ) for PUF was increased from 300 °C to ca. 340 °C when RP or MFcP was added. Load of RP or MFcP with 80 pphp or higher increased the limiting oxygen index (LOI) of PUF to higher than 25% and pass UL-94 V-0 grade. In the cone calorimetry tests (CC), It indicated that PUF/MFcP<sub>100</sub> released much less heat and smoke than PUF/RP<sub>100</sub> and PUF. The smoke release of PUF/MFcP<sub>100</sub> was reduced by almost 75% than that of PUF/RP<sub>100</sub>. The toxic gas release of PUF/MFcP<sub>100</sub> was reduced more than 50% than that of PUF/RP<sub>100</sub>. The smoke emission of PUF increased significantly after addition of RP comparing with that addition of MFcP greatly relief the situation. The corresponding mechanism was proposed.

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## 1. Introduction

Polyurethane foams (PUFs) are one of the most versatile polymeric materials because they can be formulated to meet sorts of requirements [1,2]. In addition, they are the only commercial foams which could have lower thermal conductivity than that of the air (25 mW/(m·K)) [3,4]. The rigid formulas, i.e. rigid polyurethane foams (RPUFs), are excellent building isolation materials with the second largest output [5]. However, because of the low break-up temperature of urethane bond, the thermal stability of PU products is poor indicated by their low initial and maximum decomposition temperatures [6,7]. Therefore, PUFs are highly flammable.

The well accepted FRs for PUFs are the phosphorous ones. Pristine red phosphorus (RP) itself is an effective FR for polymers even at a low loading amount, especially for oxygen-containing polymers [8–11]. Phosphorous compounds, including phosphates,

phosphonates and phosphinates, are also suggested to be flame retardants [7,12–15]. Influences of phosphorous valences have been investigated [16,17]. Lorenzetti M et al. [17] found that in the flame retardancy of rigid polyurethane foams, a combined gas and solid phase action took place at lower oxidation states of phosphorous, while only solid phase action took effect at higher oxidation states. Schartel B and his coworkers [18] further found that in the high-impact polystyrene, RP and Mg(OH)<sub>2</sub> played three different roles in the flame retardancy: (1) trapping radicals in the gas phase, (2) reducing the THE/polymer mass loss, and (3) forming a magnesium phosphates based barrier. Therefore, combination could alter the original flame resistance mechanisms of each flame retardant [19].

However, simple addition of elemental phosphorous or phosphorous salts in polymeric materials is with obvious drawbacks, such as poor compatibility with the substrates, bad water tolerance and poor handling safety. Inorganic or polymeric surface treatments are effective methods to overcome these drawbacks. Min-Jung Kim et al. [20] milled RP with graphite into graphene phosphonic acid (GPA), which showed good dispersity in polar solvents. The fire safety of the resulted paper was obviously improved. Rong-Kun Jian et al. [21] prepared encapsulated RP with polysiloxane and

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used it in polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS). The limiting oxygen index (LOI) was increased to 27.7% at a 15 wt% loading of the FR. The sample also showed excellent water resistance at a 70 °C aqueous environment for a week. Yuan Liu et al. [22] prepared capsulated RP with a coating of melamine cyanurate. PA6 with the capsulated RP possessed desired flame retardancy and showed satisfactory mechanical properties as the result of good compatibility between flame retardant and PA6. Nevertheless, it's still difficult to prevent the toxic gases of CO, NO<sub>x</sub> and HCN releasing from the combustion of PUFs. As we know, choking smoke with these strongly toxic gases is the most fatal factor of a fire [23,24]. Therefore, smoke suppression must be taken into account in flame retardant design for PUFs.

Here, we coated RP with melamine formaldehyde resin (MF) to obtain a surface coated RP (MFcP). Both kinds of phosphorous flame retardant were dispersed in polyol and foamed with isocyanate. The combustion behaviors of the resulted rigid PUFs, i.e. RPUF/RP and RPUF/MF<sub>c</sub>P, were carefully studied. With a graphitic carbon nitride coating, the mechanisms of flame resistance and smoke suppression are significantly different between RPUF/RP and RPUF/MF<sub>c</sub>P. Furthermore, the smoke and toxic gases release were significantly depressed. The results of this study are thus beneficial to further design of phosphorous flame retardant for fire safe polyurethane materials.

## 2. Experimental

### 2.1. Raw materials

Polyether polyols (4110, average functionality 4.0–4.5, OH content 430–460 mg KOH/g, viscosity 3.283 Pa·s at 25 °C, number average molecular weight 550 g·mol<sup>-1</sup>, technical grade), poly-methylene polyphenyl polyisocyanate (pMDI 44v20, average functionality 2.6–2.7, viscosity about 0.22 Pa·s at 25 °C, technical grade) and silicone oil (technical grade) were supplied by Silan trading company Ltd., Chengdu, China. Stannous octoate and Tris(dimethylaminomethyl) phenol (DMP-30, AR) were obtained from Sigma-Aldrich. PEG-400 (AR), red phosphorus (AR), formaldehyde aqueous solution (37 wt%), melamine (AR) and alkyl phenyl polyoxyethylene ether (OP-10, AR) were supplied by Chengdu Kelong Chemical Reagent Factory.

### 2.2. Preparation of MFcP

In a 500 mL beaker, 20.0 mL formaldehyde solution and 10.0 g melamine were mixed. The mixture was stirred with an overhead stirrer at the rate of 1000 r/min and kept at 40 °C for 2 h to react to prepolymer. Then 10.0 g red phosphorus and 2.0 mL OP-10 were mixed with 10.0 mL distilled water. The mixture was ground into mash in a mortar. The mash was diluted by 200 mL distilled water and added into the prepolymer. After the mixture was stirred at the rate of 1000 r/min for 5 h, the pH of solution was adjusted to 8.0 and the temperature was raised to 80 °C. The reaction was kept for 2 h before obtaining the raw product. At last, MFcP was washed with hot water to remove the residual reactant and OP-10. MFcP was kept in a vacuum oven (-0.1 MPa/80 °C) for 12 h before use. Please note: the reaction between red phosphorous and water is a potentially dangerous because the formation of PH<sub>3</sub> gas. Therefore, this reaction should be carried out in a fume hood and a personal protective gear (such as half-face respirators) are strongly recommended.

### 2.3. Preparation of PUFs

PUFs were prepared by the one-pot and free-rise method [25].

The formulations were listed in Table 1. The isocyanate index (NCO/OH in mol) was 2.0. Polyol, PEG-400, deionized water (foaming agent), silicone oil (surfactant), DMP-30, stannous octoate (catalyst), and flame retardant were mixed in a plastic beaker with a vigorous stirring of 500 r/min for 5 min. pMDI was added into the mixture soon after with a vigorous stirring of 2000 r/min for 10 s. The liquid was immediately poured into an open iron mold, which had been pre-heated to 80 °C. The first stage of cure was kept at 80 °C for 4 h, and the second stage was carried out at 120 °C for 4 h.

### 2.4. Measurement

The FT-IR spectra were recorded on a Nicolet FT-IR 170SX spectrometer using KBr pellets. The wavenumber range was from 400 to 4000 cm<sup>-1</sup>.

The morphology of RP, MFcP and PUFs was carried out with an INSPECT F scanning electron microscopy (SEM). The elements on the surface of flame retardant were detected by an INSPECT F Energy Dispersive X-Ray Spectroscopy (EDX), which was attached on the SEM.

The thermal constant of PUFs was measured by Hot Disk 2500-OT (Hot Disk, Sweden). The specimen was cut into 50 × 50 × 10 mm<sup>3</sup>.

The blind hole ratio of PUFs was measured by 3H-2000 Specific surface and pore size analyzer. The size of the specimen was 25 × 25 × 50 mm<sup>3</sup>.

Thermal gravimetric analysis (TGA) was conducted with NETZSCH 209F1 TA in nitrogen of 50 mL/min. The samples were heated to 700 °C at a heating rate of 10 °C/min.

Vertical burning tests of PUF were tested according to ASTM D 3014-04a standard. The samples were cut into 255 × 20 × 20 mm<sup>3</sup>.

The limiting oxygen index (LOI) was tested according to ASTM D2863-97 by HC-2C oxygen index instrument. The size of the specimen was 150 × 10 × 10 mm<sup>3</sup>.

A cone calorimeter (FTT, UK) in accordance with ASTM E 1354/ISO 5660-1 was used to study the combustion behavior and the gases released. The external heat flux was 35 kW/m<sup>2</sup>. The size of the specimen was 100 × 100 × 25 mm<sup>3</sup>. A FT-IR (Nicolet FT-IR 170SX spectrometer) was attached to the cone calorimeter and the peak area of a specific functional group was converted into its corresponding gas content.

The total phosphorus in the offgas of combustion was determined by the following method [16]: Quantified RPUF was completely combusted in confined conical flask which was full of pure oxygen and quantified amount of KOH/KMnO<sub>4</sub> water solution. The phosphorous gases were absorbed and oxidized. The concentration was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; IRIS Advantage, TJA solution).

The Py-GC/MS test was carried out in a combined system of pyrolyzer (CDS5200) and DANI MASTER GC-TOF-MS. Helium was used as protecting gas. Samples (about 500 μg) were heated from ambient temperature to 600 °C with a rate of 1000 °C/min and kept for 10 s before being sent into the chromatographic column. Electron impact mode (electron energy: 70 eV) was used in the MS indicator. The temperature of the ion source was kept at 180 °C.

## 3. Results and discussion

### 3.1. Morphology

The apparent morphology intuitively reflects whether the RP was coated suitably. Pristine RP and MFcP were detected by SEM (Fig. 1). Particle size of RP is ca. 30 μm, which were ground in water beforehand to lower their size distribution. Once being coated with melamine formaldehyde resin, the average size of resulted MFcP

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