



# Influence of oxidation state of phosphorus on the thermal and flammability of polyurea and epoxy resin



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## ABSTRACT

The focus of this study is an investigation of the effect of oxidation state of phosphorus in phosphorus-based flame retardants on the thermal and flame retardant properties of polyurea and epoxy resin. Three different oxidation states of phosphorus (phosphite, phosphate and phosphine oxide) additives, with different thermal stabilities at a constant phosphorus content (1.5 wt.%) have been utilized. Thermal and flame retardant properties were studied by TGA and cone calorimetry, respectively. The thermal stability of both polymers decreases upon the incorporation of phosphorus flame retardants irrespective of oxidation state and a greater amount of residue was observed in the case of phosphite. Phosphate was found to be better flame retardant in polyurea, whereas phosphite is suitable for epoxy resin. Phosphite will react with epoxy resin by trans-esterification, which is demonstrated by FTIR and <sup>31</sup>P NMR. Further, TG–FTIR and XPS studies also provide information on flame retardancy of both polymers with phosphorus flame retardants.

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## 1. Introduction

Phosphorus-based flame retardants are widely used as effective flame retardants in the form of either additives or reactives and are particularly effective in oxygen containing polymers [1–4]. There are several forms of phosphorus-based flame retardants, both organic and inorganic, and these are available in various oxidation states, including phosphines (–3), phosphine oxides (–1), elemental phosphorus (0), phosphinates (+1), phosphites (+3), phosphonates (+3), phosphates (+5), etc. In addition, several synergistic combinations are known, including, phosphorus–halogen, phosphorus–nitrogen, phosphorus–intumescent, phosphorus–sulfur and phosphorus–inorganic nano-dimensional materials [5]. Due to environmental concerns emanating from halogen-based flame retardants, more attention has been paid recently to phosphorus-based retardants. Generally, phosphorus-containing flame retardants can act either in the gas phase, by

flame inhibition, or in the condensed phase, to change the degradation pathway to one in which more char is produced and, necessarily, less volatiles. In both cases, the amount of heat released during combustion is reduced by the addition of the flame retardants [6,7].

Two reports describe the effect of oxidation state of phosphorus on the properties of carbon fiber reinforced epoxy composites and rigid polyurethane foam (PUF). Braun et al. have compared the thermal and fire retardant properties of carbon fiber reinforced epoxy with phosphine oxide, phosphinate, phosphonate and phosphate at 2.6 wt.% phosphorus content in the form of organophosphorus based curing agent. They found 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 [8]. Lorenzetti et al. have used a constant (1.2 wt.%) phosphorus content of commercially available flame retardants (aluminum phosphinate, dimethyl propane phosphonate, triethylphosphate and ammonium polyphosphate) and studied the thermal behavior in rigid PUF. There is no interaction between

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PUF and the flame retardants, irrespective of oxidation state; the higher oxidation state flame retardants showed only condensed phase action compared to lower oxidation state of phosphorus flame retardant, which function in both the condensed and vapor phases [9]. Unfortunately, in neither report was phosphite considered.

Triphenylphosphate is a classic example of a gas phase fire retardant and has been investigated by Hastie [10]. The Schartel group has compared triphenylphosphate with larger arylphosphates and found that there is more condensed phase action when the decomposition temperature increases [11,12].

In this paper, three different oxidation states of phosphorus, triphenylphosphite (+3), triphenylphosphate (+5), and triphenylphosphine oxide (−1), all with similar substituents, are studied in both polyurea and epoxy resin at 1.5 wt.% phosphorus using commercially available flame retardants.

## 2. Experimental

### 2.1. Materials

The components for polyurea preparation involve part A, diisocyanate (polycarbodiimide modified diphenylmethane diisocyanate/Isonate 143L, Dow Chemical Company) and part B, diamine (poly(tetramethyleneoxide-di-p-aminobenzoate)/Versalink P1000, Air Products). These are mixed in the stoichiometric equivalent ratio of 1:4 w/w. The epoxy resin was based on the diglycidyl ether of bisphenol-A (Araldite GY6010) and aliphatic polyether amine (Jeffamine T403) as curing agents; both are obtained from Huntsman Advanced Materials. Triphenylphosphite (Doverphos 10, P content 10%), triphenylphosphate (Reofos TPP, P content 9.5%) and triphenylphosphine oxide (P content 10%) were used as flame retardants and were received from Dover Chemicals, Chemtura and Sigma Aldrich, respectively. Benzyl dimethyl amine (BDMA),  $\text{CDCl}_3$  and 86% phosphoric acid were obtained from Sigma Aldrich as reagent grade. All chemicals were used as received.

### 2.2. Preparation of sample

The flame retardant polyurea and epoxy resin were prepared by a two-step method. At first the calculated quantity of diamine or epoxy oligomer and flame retardants (1.5 wt.% phosphorus content) were homogeneously mixed with a mechanical stirrer and then the stoichiometric amount of curatives (diisocyanate for polyurea and diamine for epoxy) was added. Finally, the resultant mixture was poured into the aluminum mold, allowed to cure at room temperature for 12 h and then post cured (70 °C/24 h for polyurea, and 80 °C/2 h, 125 °C/3 h for epoxy resin). DSC analysis confirms the complete curing (disappearance of peak exotherm) of both polymers filled with phosphorus-based flame retardants.

### 2.3. Measurements

Fourier transform infrared (FTIR) spectra were performed on a Bruker TENSOR 27 spectrophotometer from

4000 to 600  $\text{cm}^{-1}$  using ATR mode.  $^{31}\text{P}$  NMR spectra were obtained using 10–25% solutions in deuteriochloroform ( $\text{CDCl}_3$ ) on a Varian 400 NMR (400 MHz) spectrometer. The phosphorus chemical shifts are relative to an external 86% aqueous phosphoric acid solution as reference.

The thermal stability of sample was measured on a SDT Q600, (TA Instruments) under a nitrogen (gas flow of 100 mL/min) atmosphere at a scan rate of 20 °C/min over a temperature range of 50–800 °C. Typical sample weights of 5–10 mg were employed. All samples were run at least in duplicate; temperature is reproducible to about  $\pm 2$  °C and mass to 0.2%.

The TGA–FTIR analysis was performed using a Netzsch TG 209 F1 Iris coupled to a Bruker Tensor 27 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 20 °C/min over a temperature range of 30–700 °C. The sample weight was around 5 mg. The coupling system between the TG and FTIR was maintained at 200 °C to prevent condensation of the evolved gases.

The flame retardant properties were measured using a cone calorimeter (Atlas Cone 2) according to ASTM E1352 at a heat flux of 50  $\text{kW/m}^2$ . The specimens for the cone calorimetric analysis were 100 mm  $\times$  100 mm  $\times$  6 mm (length  $\times$  width  $\times$  thickness) and three specimens per sample were measured and average values are reported. The results from cone calorimeter are generally considered to be reproducible to  $\pm 10\%$ .

The elemental composition of the decomposed residue was analyzed using X-ray photoelectron spectroscopy (XPS), carried out on a PHI Quantera-II SXM (Ulvac-PHI, Inc.) using Al K $\alpha$  radiation and an X-ray power of 2.5 kW under a vacuum of  $2.6 \times 10^{-7}$  Pa. The pass energy is 280 eV and the step length is 1 eV with a takeoff angle at 45°.

## 3. Results and discussion

The rapid linear polycondensation (without removal of by-products) of elastomeric polyurea (PU) without external catalyst and the ring opening condensation polymerization (without removal of by-products) of amine cured epoxy resin (EP) formation (a) and the chemical structure of different oxidation state of commercially available phosphorus flame retardants include triphenylphosphite [TPPi, (b)], triphenylphosphate [TPP<sub>a</sub>, (c)] and triphenylphosphine oxide [TPPO, (d)] are shown in Fig. 1. In the case of PU, the molecular chains are physically cross-linked microphase separated block copolymers of dispersed short oligomeric MDI hard segments aggregated through hydrogen bonds in the continuous long amorphous matrix of flexible (soft) segments, made of the high molecular weight diamine, that give extensibility to the PU. Interactions between chains, mainly hydrogen bonds between hard segments acting as a reinforcing filler, contribute to the properties of PU [13]. For EP, the hard and three-dimensional network structure is formed after chemical (amine) crosslinking at elevated temperature.

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