



## Effect of phosphorous-modified silica on the flame retardancy of polybutylene terephthalate based nanocomposites



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### ABSTRACT

The effect of silica treatment by three phosphorous compounds (phosphoric acid, dihydrogen ammonium phosphate and diammonium phosphate) on the thermal and fire behaviour of polybutylene terephthalate (PBT) composites was investigated using Thermogravimetric analysis (TGA), Pyrolysis Combustion Flow Calorimeter (PCFC) and cone calorimeter. It was found that with only 10 wt% of treated silica incorporated into PBT, which corresponds to only 0.2 wt% of phosphorus in composites, the fire behaviour of materials was dramatically improved with a 60% decrease of peak of Heat Release Rate (pHRR). The incorporation of modified silica also leads to a fire growth rate index of 4.3 kW/(m<sup>2</sup>.s) (i.e. a 40% decrease). Those phenomena were related to the expansion of composites during their combustion and to their rheological behaviour. Indeed, the higher the viscosity at low frequencies is, the better the fire behaviour is, due to the induced barrier effect. A decrease of time to ignition (TTI) was also observed with the addition of the various silicas (up to 18s with 10 wt% of neat silica), which was explained by the appearance of bubbles after the PBT melting during cone calorimeter tests leading to a fast increase of the surface temperature.

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## 1. Introduction

Polybutylene terephthalate (PBT) is an engineering thermoplastic polymer which exhibits very good heat resistance and electrical insulation properties. Thus PBT is an interesting solution for a wide range of industrial applications such as automotive parts, connectors for electronics, electrical components, cable jackets ... Many of these applications dictate stringent specifications with regard to reaction-to-fire and require PBT to be flame retarded.

Historically, flame retardancy of PBT was achieved by using halogenated compounds such as brominated carbonate, brominated polystyrene or brominated phosphate ester [1,2]. From the early 2000s and notably due to the restriction of some hazardous substances in electrical and electronic equipment, efforts have been devoted to find non-halogen flame retardant (FR) for PBT. The main envisaged alternatives have been nitrogen- and above all phosphorus-containing compounds.

Levchik et al. [3] studied a series of phosphazenes and derivatives to improve the fire behavior of PBT. Some of the tested FRs were shown to promote charring. However no relation was found between char promotion and fire performance, *i.e.* limiting oxygen index (LOI) and UL94 rating, indicating the poor efficiency of the char layer. The best results were obtained by combining phosphazene with charring polymers like poly(phenylene oxide). Two years later, Levchik et al. [4] tested a similar approach with different aryl phosphates as FRs. It was highlighted that aryl phosphates alone do not have a strong effect on flame retardancy of PBT since they do not promote charring. Moreover they tend to exude from the host polymer. Balabanovich [5] showed that a high loading (30 wt%) of bisphenol-A bis(diphenyl phosphate) (BDP) is required to give a significant stable residue and thus an increase in LOI. Nevertheless, aryl phosphates can lead to better results when associated with co-synergist agent. For example, BDP or resorcinol bis(diphenyl phosphate) (RDP) associated with novolac phenolic resin (25 wt% total loading) give an improvement of UL94 rating (V-0) due to the formation of an intumescent char at the surface of the sample [4]. Xiao et al. [6] showed a synergism between triphenyl phosphate (TPP) and melamine (MA). In this case, it was concluded that the FR

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system acted both in the vapor and condensed phase and enabled V-0 rating with a global additive loading of 30 wt%. Balabanovich [7] evidenced that MA alone can improve the fire performance of PBT by promoting the formation of a solid residue consisting of condensation products of MA. However a 40 wt% loading is needed to obtain 26% LOI and a V-0 rating at UL94 test. Another strategy to improve UL94 rating at lower FR loading consists in combining the use of a phosphorus compound and PBT crosslinking. This was achieved by Balabanovich [8] using red phosphorus and triallyl cyanurate (TAC) as crosslinking promoter under  $\gamma$  irradiation. With 12.5 wt% red phosphorus and 3 wt% TAC, dripping was inhibited and thus V-1 rating was obtained. In the same vein, Gao et al. [9] synthesized a novel nitrogen-phosphorus containing intumescent FR that was likely to provoke crosslinking reaction during thermal degradation and therefore to increase the char yield of PBT.

During the last decade, phosphinates have been the phosphorous chemicals that rouse the main interest as FR for PBT. First works were published by Balabanovich et al. [10] that associated 2-methyl-1,2-oxaphospholan-5-one 2-oxide (OP) with ammonium polyphosphate (APP) for the flame retardancy of PBT. V-0 rating was obtained with 15 wt%APP and 10 wt% OP due to a condensed phase mechanism that promotes charring and gives an intumescent effect. Thereafter the group of Schartel at BAM undertook several studies involving metal (zinc and aluminium) phosphinates as FR for PBT. It was highlighted that phosphinates act both in the condensed and gas phase [11]. In the gas phase, whatever the metal ion, the release of phosphorous species induces flame inhibition as proved by the higher CO production. In the condensed phase, despite a moderate increase in char yield, the presence of phosphinate induces a strong barrier effect that was assigned to the particular structure of the residue. Aluminium salt was proved to be more efficient than zinc salt [12]. In order to enhance its performance, aluminium phosphinate (AlPi) was also tested in combination with melamine derivatives [13,14] or montmorillonite [15].

Despite the large literature on oxide particles and nanoparticles as component of flame retardant systems, this strategy was rarely investigated in the PBT matrix. Gallo et al. [16] studied the influence of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles on the fire behavior of PBT. The best results were obtained when oxides are combined with aluminum phosphinate. Phosphinate acts mainly in the gas phase while mineral nanoparticles were evidenced to have a condensed-phase action. Oxides were supposed to stabilize the polyester matrix by Lewis acid/base interactions and thereafter to promote its charring. This enabled conferring satisfying fire performance with a limited amount of additives.

Since the early works of Kashiwagi et al. [17–19], silica has been the most studied oxide for flame retardant applications. Highly porous silica was shown to slow down the decomposition kinetics of polymers due to molecular mobility restriction and trapping of decomposition products. Silica may also modify the viscoelastic properties of decomposing polymer and favor the formation of a protective layer at the sample surface. Silica was used also as synergist in intumescent FR system where it enabled reinforcing the char layer [20,21]. Silica was also claimed to act as smoke suppressant [22]. In order to combine the intrinsic effect of silica with the effect of a char layer, attempts have been made to prepare phosphorus-modified silica particles. In the literature, two routes may be distinguished: (i) the chemical modification of preformed silica particles, (ii) the one-step synthesis of modified silica by the so-called sol-gel process. Concerning this latter route, phosphorus-doped silicas were obtained using alkoxysilane precursors bearing a phosphorous group. This was achieved either before material processing [23] or in-situ during polymer extrusion [24–26]. With regard to the functionalization of preformed fillers, Dong et al. [27] achieved the immobilization of 9,10-

dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) on silica nanoparticles. Once incorporated in polypropylene in combination with an intumescent FR system, this modified silica was proved to improve flame retardancy [28]. In a previous paper [29], we performed the grafting of phosphorous moieties onto highly porous silica particles using an alkoxysilane bearing a phosphate group. The modified silica was evidenced to increase the thermo-oxidative stability of polypropylene. The performance in cone calorimeter test was shown to be tightly related to the viscosity of the polymer. However the phosphorus-containing silica was unable to promote any char and thus its interest remained limited in a non-charring matrix.

In this work, a similar approach was adopted for the fire-proofing of PBT, a charring polymer. Precipitated silica was surface modified by different phosphorous compounds and then incorporated in the polyester matrix. The thermal and fire behaviors were characterized. Efforts were made to elucidate the different modes of action of phosphorus-modified silica used as FR.

## 2. Experimental

### 2.1. Materials and reagents

Silica Zeosil 1165 MP (Z) was provided by Solvay. This silica is a micropearl that consists of an agglomeration of primary spherical particles of about few nanometers in diameter. The micropearl size of this silica is 250  $\mu\text{m}$ , its BET surface area is 173  $\text{m}^2/\text{g}$  and silica Z has a porosity equal to 3.13  $\text{cm}^3/\text{g}$ . Phosphoric acid (PA) and dihydrogen ammonium phosphate (DHAP) from Sigma Aldrich and diammonium phosphate (DAP) from Carlo Erba were used as flame retardant agents for the silica surface treatment. PBT (PBT Crastin<sup>®</sup> S600F40 NC010) was supplied by DuPont<sup>™</sup>. This PBT has a low viscosity and is lubricated. Its Melt Flow Index and melting point are 32.9 g/10 min (250 °C, 2.16 kg) and 225 °C respectively. All these products were used as received without further purification.

### 2.2. Preparation of modified silicas

Precipitated silica Z was modified with PA, DHAP and DAP (respectively named ZmPA, ZmDHAP, ZmDAP). In all cases, 100 g of dried silica Z were dispersed in 1 L of anhydrous ethanol with 11.1 g of treatment agents [30]. After 5 h of reaction under reflux, solvent was removed by evaporation and the resulting solid was dried at 80 °C overnight in vacuum.

### 2.3. Preparation of PBT composites

Prior to melt processing, PBT pellets were dried at 80 °C overnight in a vacuum oven. 10 wt% of neat silica Z or modified silica were incorporated into dried PBT using a Leistritz LSM30-34 (D = 34 mm, L/D = 34) co-rotating twin-screw extruder at a temperature of 240 °C. The rotation speed was kept to 150 rpm and polymer feed rate was 3 kg/h. Then composites were granulated and injection molded at 240 °C with a mold temperature equal to 60 °C using 50 Krauss-Maffei apparatus (Munich, Germany) to obtain samples with dimensions 100 × 100 × 4  $\text{mm}^3$ .

### 2.4. Characterization

#### 2.4.1. Elemental analysis

Elemental analysis was carried out at the Institut des Sciences Analytiques (ISA, CNRS, Villeurbanne). Silicon and Phosphorus contents were determined by ICP-AES (inductively coupled plasma-atomic emission spectrometer) and carbon content by either catharometry or specific infrared detectors.

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