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A comparative study of POSS as synergists with zinc phosphinates for PET fire retardancy

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ABSTRACT

This paper deals with the fire behaviour of poly (ethylene terephthalate) (PET) filled with Exolit OP950, a zinc phosphinate fire retardant, and three polyhedral oligomeric silsesquioxanes (POSS) having different chemical structures. Regardless of the POSS type, intumescence occurs during combustion, but the insulation properties of the chars produced are different. Best reductions on total heat evolved (THE) and on cumulative CO_2 with no increase in CO emissions are observed when dodecaphenyl POSS is used. This may be related to its thermal degradation pathway, releasing via this process volatile organic species contributing on intumescence and producing an effective protective layer having a foliated structure.

1. Introduction

Thanks to its easy processability, low cost and good mechanical and chemical properties, poly(ethylene terephthalate) (PET) use is in constant growth for various applications. This material can be found in numerous forms as injection-moulded articles, clothing or upholsteries. Nevertheless, it may constitute a potential high hazard as it poorly withstands elevated temperatures and would feed fire by playing the role of fuel. That is why several works were led to enhance the fire resistance of this thermoplastic polymer [1–7].

Looking for synergistic effects between fire retardant (FR) additives is of great interest since halogen-containing chemicals were banned due to their toxicity [8–10]. Developing polymer nanocomposites (thermoplastic or thermoset materials blended with nanofillers) is a preferred way for synergisms as reflected by the recent advances in this field [10–12].

Polyhedral oligomeric silsesquioxanes (POSS) [13–15] are hybrid particles in a cage-like shape combining inorganic and organic moieties where silicon and oxygen form a core surrounded by functional groups. Silsesquioxanes have been studied for polymers fire properties enhancement. Fina et al. [16] investigated pyrolysis and thermal oxidation of virgin polypropylene (PP) and its derivates containing POSS. Results showed that the introduction of the nanoparticles enhances the thermoxidative stability of PP. The same authors [17] led a complementary study to determine the fire behaviour of the materials and succeed to lower the heat release rate (HRR) of 40% when PP is loaded at 10 wt.% with an aluminium containing POSS. Devaux et al. [18] used TPU (thermoplastic polyurethane)-POSS composites as coating for PET fabrics and observed a 50% HRR reduction of the whole material with 10 wt.% of POSS addition while Bourbigot et al. [19] studied the fire resistance of TPU-POSS alone and observed a decrease of HRR peak by 80% compared to virgin TPU.

Concerning synergistic effects between fire retardants and POSS, only few works are published even though this way presents advantages as reducing the amount of POSS which are expensive components. Chigwada et al. [20] reached high reduction of HRR peak when POSS and phosphates are introduced in vinyl ester resin. Also, Vannier et al. [21–23] showed synergistic effects in fire retardancy by melt mixing phosphorus-containing additives (Exolit OP950) and OctaMethyl POSS (OM-POSS). Nanoparticles addition of only 1 wt.% enhances the intumescence mechanism of the filled thermoplastic polymers.

Fina et al. [14] conducted a comparative study on the thermal stability of different POSS and showed that their thermo-oxidative behaviours depend on their functional groups presenting residual

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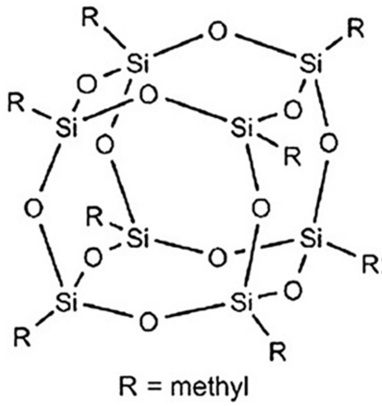

Fig. 1. OM-POSS (OctaMethyl POSS).

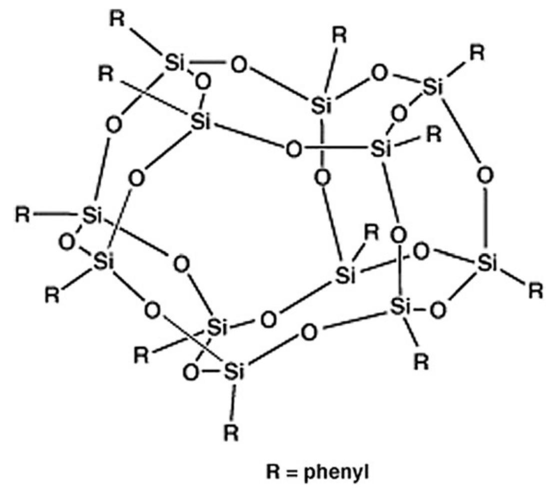

Fig. 3. DP-POSS (DodecaPhenyl POSS).

masses at high temperatures under thermogravimetric analyses going from 93% to 17%. We conducted a comparative study of fire retardancy between an established Exolit OP950/OM-POSS results and other blends containing zinc phosphinates and POSS having different surrounding moieties. Electronic microscopy was used to examine the morphology of loaded matrices. Thermogravimetric analyses were carried out in order to investigate potential synergisms on thermal stability between the additives and PET. The materials were also characterized by cone calorimeter to analyse their fire behaviour.

2. Experimental

2.1. Materials

Commercial grade of PET (SABIC, TC196) chips and POSS nanoparticles were purchased respectively from Sabic and Hybrid Plastics Company. Exolit OP950, the zinc phosphinate compound, was kindly supplied by Clariant. The three selected POSS were OctaMethyl POSS (OM-POSS, Fig. 1), poly(vinylsilsesquioxane) also called Fire Quench POSS (FQ-POSS, Fig. 2) and DodecaPhenyl POSS (DP-POSS, Fig. 3).

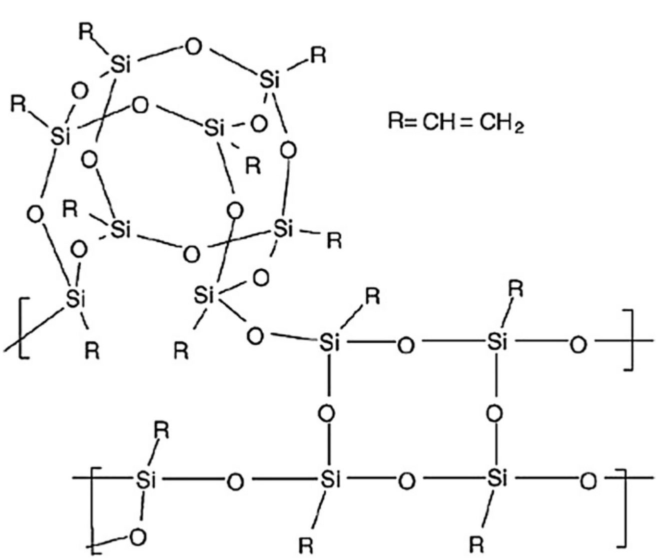

Fig. 2. FQ-POSS (Fire Quench POSS) [19].

- OctaMethyl POSS and its synergism with OP950 was already studied and discussed [21]
- Fire Quench POSS is assessed to have improved thermal and flame retardant properties [19]
- DodecaPhenyl POSS is not mentioned in literature for flame retardancy aspects but we selected it assuming that its phenyl groups may render it thermally stable, which is preferable to withstand processing temperatures of PET.

2.2. Processing

Pellets, additives and loaded chips were dried 12 h at 80 °C before extrusion and compression moulding processings. The formulations (Table 1) were melt blended using a co-rotating twin-screw extruder (Thermo Haake, diameter of screw = 16 mm, L/D = 25). The temperatures of the five zones were respectively 260 °C/260 °C/258 °C/254 °C/248 °C), and the rotation speed was maintained at 100 rpm. The rods obtained were then pelletized, and the chips were transformed in sheets using a Dolouets heating press at 265 °C under 50 bars.

2.3. Scanning electron microscopy

Images were taken using a Phillips XL40 scanning electronic microscope in order to analyse the dispersion of the nanofillers in PET matrix.

Table 1
Composition of the materials.

Designation	Extruded chips				
	PET	PET-OP 10	PET-OP-OM 9-1	PET-OP-FQ 9-1	PET-OP-DP9–1
PET (wt.%)	100	90	100	90	90
Exolit OP950 (wt.%)	0	10	9	9	9
OM–POSS (wt.%)	0	0	1	0	0
FQ-POSS (wt.%)	0	0	0	1	0
DP-POSS (wt.%)	0	0	0	0	1