



## Catalytic fire retardant nanocomposites

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### ABSTRACT

In this paper the chemical activity of carbon nanotubes and polyhedral oligomeric silsesquioxane during thermal degradation and combustion of polymer nanocomposites is addressed. Indeed, polymer–nanofiller systems may exhibit chemical effects capable of thermal stabilisation of polymers as well as reduction of combustion rate and heat released, owing to catalytic effects induced by the nanofillers at high temperature.

Carbon nanotubes in the presence of oxygen are shown to promote oxidative dehydrogenation in polyethylene with production of a stable surface layer of carbon char that provides an effective oxygen barrier effect. A similar action is performed by metal-containing polysilsesquioxanes dispersed in polypropylene.

With either carbon nanotubes or metal POSS, partial carbonisation of the polymer matrix occurs during combustion, subtracting part of the organic polymer from combustion, targeting one of the major fire retardancy aim.

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### 1. Introduction

The flammability of polymers still represents the most important limitation in their use because of the related fire risk (probability of fire occurrence) and hazard (consequences of a fire) in a number of industrial applications of polymer materials, including electrical–electronic (E&E) sector, transport, building and furniture. The concern about environmental and health safety for traditional halogenated Fire Retardants (FRs) has driven new European regulations progressively restricting their use since the year 2000, leading to the ban of some halogenated compounds (e.g. penta- and octa-bromodiphenyl ether), whereas some other FRs are currently undergoing a very thorough risk assessment procedure. Moreover, the use of brominated fire retardants is discouraged by the Directive 2002/96/EC of the European Parliament on waste electrical and electronic equipment (WEEE) requiring separation of brominated fire retarded plastics from E&E equipment prior to recovery and recycling which has become mandatory for end of life electrical and electronic equipments. Further limitations to the use of halogenated fire retardants come from the directive on Restriction of the use of Hazardous Substances (RoHS) and from the REACH regulation. Although some halogenated fire retardants have been recognised safe for health and environment on the basis of an

extensive risk assessment, the general feeling in the industry of materials' production and end users is that halogen-free fire retardants should be developed, showing at least the same effectiveness of halogenated systems.

In the research effort to find new environmental friendly fire retardants, inorganic nanofillers emerged as promising solution to polymer fire retardancy, because these typically induce a dramatic reduction of the combustion rate compared with the corresponding polymer matrix at relatively low loadings (e.g. 5 wt.%), simultaneously improving physical and mechanical properties.

The first nanoparticles being used as fire retardants were the so-called nanoclays: indeed, clay–nanocomposites were shown to have beneficial effects on combustion, owing to the formation of a protective surface layer composed of a thermally stable combination of carbonaceous char and clays [1–5], as a consequence of polymer ablation.

Carbon nanotubes (CNTs) were already used to reduce flammability properties of several polymer materials [6–11], showing a general reduction of combustion rate. Fire retardance of polypropylene/multi-wall CNT (MWNT) nanocomposites was studied in detail by Kashiwagi et al. [6–8] who observed that during combustion a nanotube network layer is formed which insulates the PP from the external radiant flux, changing the transmission of heat from thermal conduction to radiative transfer. The nanotube layer becomes a physical shield decreasing external heat flux by one half. Scharrel et al. obtained similar conclusions in polyamide-6 (PA-6)/MWNT [9], reporting the formation of MWNT interconnected

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**Table 1**  
MWNT description

Property	
Average diameter (nm)	10
Length ( $\mu\text{m}$ )	0.1–10
Carbon purity (%)	90
Metal oxides ( $\text{Al}_2\text{O}_3$ ) (%)	10

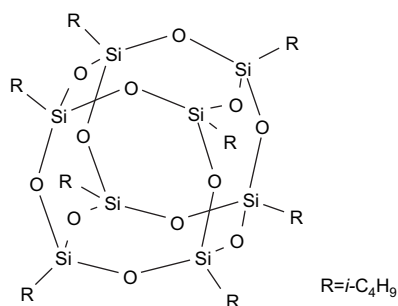
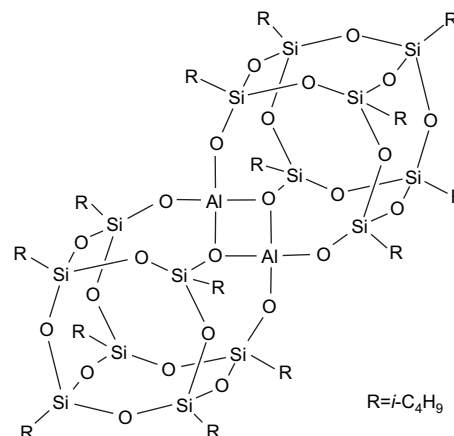
network structure during burning, responsible of a melt viscosity increase preventing dripping and flowing of the nanocomposite during burning.

Kashiwagi et al. [8] also studied the effect of single wall CNTs (SWNTs) dispersion on fire retardant properties for poly(methyl methacrylate) evidencing a direct correlation with the formation of an analogous thermal protective layer as a function of nanotubes' dispersion in the polymer matrix. Similar results were obtained by Bourbigot et al. [10] who reported a decrease of mass loss rate during radiative gasification test of well-dispersed MWNT–PS nanocomposite with respect to sample containing MWNT roughly dispersed.

The use of polysilsesquioxanes as flame retardants has been explored as well [12–14], showing benefits during combustion, due to the accumulation of a ceramic layer on the surface of the burning material by silsesquioxane thermal degradation [15,16] resulting in a physical protective barrier, strongly decreasing the combustion rate. Among silsesquioxanes, polyhedral oligomeric silsesquioxanes (POSS) were also addressed [17–19], which are attractive because of their strictly controlled and tailorable structure. However, POSS volatilisation should be taken into account for certain POSS structures [16], which obviously affects the ceramic yield during combustion, thus possibly leading to limited effects in fire behaviour.

In the cases described so far, a purely physical effect of the nanofiller has usually been proposed, related to the formation of a carbonaceous or ceramic layer by the accumulation of inorganic particles on the surface, acting as a physical barrier, shielding the underlying polymer from the radiated heat and limiting polymer ablation, thus reducing the amount of combustible volatile products available for burning in the gas phase. However, some aspects of nanocomposite combustion have still to be modified to make them suitable as a general approach to fire retardancy, particularly as regards to ignition delay time and flame persistency [20,21]. Indeed, polymer nanocomposites often show a shorter time to ignition when exposed to an ignition environment, as compared with reference polymer [22]. Moreover, despite the reduction of combustion rate, self-extinguishing of polymer nanocomposites remains to be achieved: the persistency of a small flame is usually observed during vertical self-sustained flammability tests (e.g. LOI, UL94) preventing attribution of fire retardant classification which is required by materials' applications.

In order to overcome the present limitations, the combination of a chemical action with the physical effect of inorganic nanoparticles

**Fig. 1.** Octaisobutyl POSS structure (oib-POSS).**Fig. 2.** Al-POSS structure.

appear to be the most promising way to develop fire-safe environmental friendly polymeric materials.

The combination of nanofiller and a non-halogenated fire retardant has been explored for a few different systems [23,24], showing additive or synergistic effect of the nanofiller and the fire retardant, leading to fire retardancy performance complying with commercial standards which are not met so far by the corresponding nanocomposite. This is most likely related to a coupling of the barrier effect due to the nanofiller and the chemical action brought about by the fire retardant; however, chemical and physical mechanisms of interaction need to be assessed. The designed coupling of nanofiller and fire retardant moieties is expected to result in a significant advance, based on the results of the mechanistic study of nanofiller–fire retardant synergism.

A more effective strategy to combine nanofiller and halogen-free fire retardant in synergic formulations is the functionalisation of nanofillers with FR-active moieties. Thanks to their versatility, carbon nanotubes (CNT) and polyhedral oligomeric silsesquioxanes (POSS) appear to be the most appealing nanoparticles to be functionalised to get intrinsically fire retardant action.

In this paper, the chemical activity of carbon nanotubes and polyhedral oligomeric silsesquioxane during thermal degradation and combustion is addressed.

## 2. Experimental

### 2.1. CNT-nanocomposite preparation

Polypropylene, highly isotactic, semi-crystalline, nucleated homopolymer, Moplen HP500N (PP), linear low-density polyethylene, Lupolex 18Q FA (PE) and poly-1-butene, highly isotactic, semi-crystalline, nucleated homopolymer, PB 0110 (PB) were supplied by Basell. Multi-Wall Nanotubes (MWNT) Nanocyl<sup>®</sup>-7000 supplied by Nanocyl were used, properties of which are summarized in Table 1.

MWNT nanocomposites were prepared adding 3 wt.% MWNT to polymers via melt-blending using a Brabender Plasticorder PLE851 internal mixer at 180 °C for PP, 160 °C for PB and 120 °C for PE, 60 rpm for 8 min. Specimens for cone calorimeter were prepared by hot pressing using a hydraulic press with the two plates heated at 190 °C for PP, 170 °C for PB and 130 °C for PE using a pressure of 25 bar for 5 min.

### 2.2. POSS-nanocomposite preparation

Octaisobutyl-T<sub>8</sub>-POSS, (*i*-C<sub>4</sub>H<sub>9</sub>)<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> (Fig. 1), referred to as oib-POSS in the following, was purchased from Hybrid Plastics Company and used as received. Al-containing POSS (Al-POSS) (Fig. 2) was prepared by deprotonation of incompletely condensed POSS

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