Available online at www.sciencedirect.com

Polymer Degradation and Stability 91 (2006) 2275–2281

Polymer Degradation and Stability

www.elsevier.com/locate/polydegstab

Metal functionalized POSS as fire retardants in polypropylene

Alberto Fina [a,*], Hendrikus C.L. Abbenhuis [b], Daniela Tabuani [a], Giovanni Camino [a]

[a] *Centro di Cultura per l'Ingegneria delle Materie Plastiche – Politecnico di Torino, V.le T. Michel, 5 – 15100 Alessandria, Italy – and INSTM member*
[b] *Eindhoven University of Technology, Hybrid Catalysis BV, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

Received 20 March 2006; received in revised form 18 April 2006; accepted 24 April 2006

Abstract

This paper deals with the study of the combustion properties of dimeric and oligomeric Al-and Zn-isobutyl silsesquioxane (POSS)/polypropylene (PP) composites, in comparison with neat PP and PP/octaisobutyl POSS.

The presence of Al-POSS leads to a decrease in combustion rate with respect to PP, resulting in a decrease of Heat Release Rate (−43% at 10 wt% POSS loading) as well as reduction in CO and CO_2 production rates, whereas a negative effect on the above parameters is obtained with octaisobutyl POSS. Zn-POSS does not significantly affect the PP combustion behaviour.

The effect of Al-POSS is most likely related to its chemical activity, which favours the formation of a moderate amount of char residue, by catalysing secondary reactions in the polymer during combustion.

Keywords: POSS; Polysilsesquioxane; Flame retardancy; Metal-POSS; Cone calorimeter; Combustion

1. Introduction

In recent years, much effort was dedicated to the development of halogen free flame retardants for polymers, in order to avoid the use of traditional chlorinated or brominated compounds; in this field, attention was given to silicon containing flame retardants such as silanes, siloxanes and silsesquioxanes [1,2]. These compounds are recognised to be the precursors for the formation of thermally stable ceramic materials so that they are also referred as preceramic compounds.

Different polysilsesquioxane or polycarbosilane resins were shown to be effective fire retardants in thermoplastic polymers such as polypropylene (PP), styrene-butadiene-styrene block copolymers (SBS) and polyether-polyamide copolymers (PTME-PA), by reducing the Heat Release Rate during cone calorimeter tests [3,4]. In PP a 40% reduction in Heat Release Rate (HRR) peak was obtained with 20 wt% of a methyl/phenyl polysilsesquioxane and even better results were obtained in PTME-PA, with HRR peak reduction of about 70% by incorporation of 10 wt% of the same polysilsesquioxane. The proposed mechanism of fire retardancy with preceramics involves the formation of an insulating char, which shields the underlying polymer from the radiated heat and limits polymer ablation, thus reducing the amount of combustible volatile products available for burning in the gas phase [4].

Few scientific papers have been published so far on the use of Polyhedral Oligomeric Silsesquioxane (POSS) as flame retardants.

Ikeda reported the use of POSS, with different cage structures and organic substituents, in polyphenylene ether (PPE), showing the formation of a tough foam layer on nanocomposite surface during UL94 tests, leading to V0 classification, whereas neat PPE was classified as V1 [5].

Bourbigot et al. prepared polyurethane/POSS (TPU–POSS) nanocomposite coatings for textiles and tested knitted multifilament yarns on cone calorimeter. TPU–POSS coating on polyester woven fabrics resulted in a remarkable reduction of the Heat Release Rate peak (up to 50%), in particular with the use of

---

[*] Corresponding author. Tel.: +390131229316; fax: +390131229331.
E-mail address: alberto.fina@polial.polito.it (A. Fina).

0141-3910/$ - see front matter
doi:10.1016/j.polymdegradstab.2006.04.014

phenyl-T_{12} POSS and with poly(vinyl silsesquioxane) resin, whereas methyl-T_8-POSS was found to be almost ineffective [6,7]. The same research group also prepared multifilament yarn knitted fabric with PP/poly(vinyl silsesquioxane) resin nanocomposites, showing an increase of the Time to Ignition with no significant effects on the Heat Release Rate [7].

Recently, combustion behaviour of a PMMA–trisilanol phenyl POSS nanocomposites was studied by means of cone calorimeter tests, showing no improvements with respect to neat PMMA [8].

As regards thermoset polymers, interesting results were obtained on vinyl ester resins by the addition of vinyl POSS [9,10] in terms of reduced smoke release, lower HRR and higher ignition time, with respect to neat resin.

Synergic formulations with phosphorous-based fire retardants were recently studied in vinyl ester thermoset nanocomposites [11]. Significant reductions of the HRR peak were obtained with vinyl POSS and an improvement was achieved by the addition of tricresylphosphate, also leading to important reductions of the Total Heat Released.

The effect of metal nanoparticles on polymer flammability was explored by Antonov et al. [12], showing that finely dispersed metals at low concentration ($\leq$1 wt%) strongly enhance PP char yield, by catalysing dehydrogenation, despite a higher flammability, shown by lower LOI values.

Since the possibility to remove part of the organic polymer from combustion through carbonisation is one of the main goals in polymer fire retardancy [13], the dehydrogenation effect appears to be particularly interesting.

In this work the effect of metal-containing POSS on PP combustion behaviour was investigated; such compounds were chosen to couple the silsesquioxane preceramic effect with the catalytic action of a metal site on POSS cage, taking advantage from the possibility to disperse POSS cages on a submicron scale into polymer matrix [14]. These systems have been previously investigated by the same authors, showing that thermoxidative degradation of composites is strongly affected by the presence of metal-containing POSS, resulting in an improved thermal stability, in terms of higher weight loss temperature [15].

2. Experimental

Octaisobutyl-T_8-POSS, $(i\text{-}C_4H_9)_8Si_8O_{12}$, (Fig. 1), referred to as T_8-POSS in the following, was purchased from Hybrid Plastics Company and used as received.

Metal-POSS derivatives (Al-POSS and Zn-POSS, Figs. 2 and 3, respectively) were prepared by deprotonation of incompletely condensed POSS trisilanol, $(i\text{-}C_4H_9)_7Si_7O_9(OH)_3$ with either triethylaluminium or diethylzinc as previously reported [15].

PP was a Moplen HP501L, purchased from Basell.

Composites were prepared by mixing PP and POSS in a Brabender internal mixer (180 °C, 20 min, 60 rpm); these blending conditions were chosen on the basis of what reported by Fu et al. [16] and on our previous work [14]. POSS was loaded into the polymeric matrix at 10 wt% ratio. Neat PP was processed in the same conditions as a reference material.

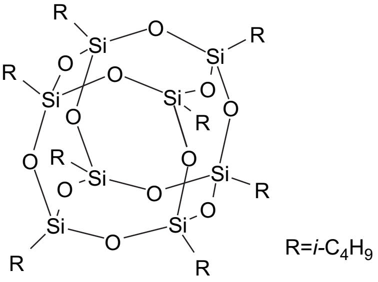

Fig. 1. Octaisobutyl POSS (T_8-POSS).

Combustion tests were performed on a Fire Testing Technology Cone Calorimeter, with 100 × 100 × 3 mm specimens, prepared by compression moulding on a hot plate laboratory press at 190 °C and conditioned at 23 °C and 50% RH to equilibrium.

Tests were performed at 35 kW/m^2 external heat flux, in order to evaluate the fire properties of the composites in conditions comparable to a mild fire scenario [17]; specimens were wrapped in an aluminium foil leaving the upper surface exposed to the radiator and placed on ceramic backing board at a distance of 25 mm from cone base.

Three tests for each sample were performed and in the following section the average values will be discussed; data are reported with their deviation with respect to the average.

Raman spectra using 633 nm excitation wavelength were recorded on a Jobin Yvon Labram HR spectrophotometer, equipped with an Olympus microscope and using a CCD detector, using a 1800 lines/mm grating, determining a instrumental resolution of 2.5 cm^{-1}, with typical laser power set at 10 mW.

Scanning electron microscopy imaging was obtained by means of a LEO 1450 VP instrument on cryogenic fracture surfaces.

3. Results and discussion

The main parameters obtained from cone calorimeter measurements are reported in Table 1 for each material and will be

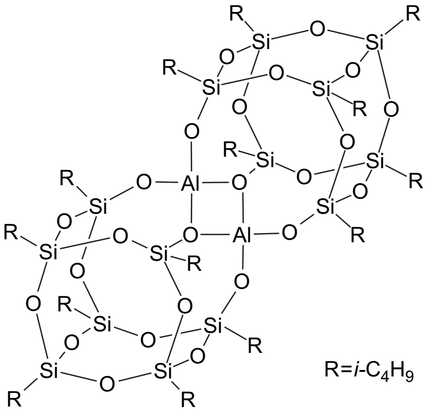

Fig. 2. Al-POSS.