DOI: 10.1002/ejic.200600683

Synthesis and Characterisation of Metal Isobutylsilsesquioxanes and Their Role as Inorganic–Organic Nanoadditives for Enhancing Polymer Thermal Stability

Fabio Carniato,[a] Enrico Boccaleri,*[a] Leonardo Marchese,[a] Alberto Fina,[b] Daniela Tabuani,[b] and Giovanni Camino[b]

Dedicated to the memory of Roberto Piazza[†]

Keywords: Silsesquioxanes / Titanium / Vanadium / Polymers / Nanocomposites

Metal isobutylsilsesquioxanes (M-POSS) with Ti^{IV} and V^{V} metal centres have been prepared by direct corner-capping of trisilanolisobutyl-POSS (**1**). The synthetic procedure has been followed in solution by FTIR spectroscopy and samples have been characterised by $^{29}Si\{^{1}H\}$ NMR, FTIR, FT-Raman and UV/Vis spectroscopy in order to study the structure and the chemical properties of the transition metal centres incorporated in the synthesised compounds. The corner-capping reaction basically lead to tetrahedrally coordinated metal centres inserted in the siliceous cage. The hybrid inorganic–organic nature of these compounds and the possibility of dispersing catalytically active metal centres in a highly efficient way within organic matrices have been investigated by dispersing the title compounds at 3 wt.-% in a polypropylene matrix by melt blending, which leads to nanocomposite materials. A study of the thermal degradation of polypropylene, trisilanolisobutyl-POSS and metal-isobutyl-POSS composites shows a significantly enhanced thermal stability under oxidative conditions only when metal-containing silsequioxanes are dispersed, along with an extended formation of condensed polyaromatic compounds (charring products). This evidence is consistent with a possible catalytic effect favouring oxidative dehydrogenation of the polymeric organic chains occurring in the condensed phase under combustion conditions, and highlights a possible promising use of M-POSS as fire-retardant additives for polymers.

Introduction

Polyhedral oligomeric silsesquioxanes (POSS) are a class of condensed, three-dimensional oligomeric organosilica compounds with cage frameworks having different degrees of symmetry. These materials are present in most of the up-to-date research topics in the field of advanced materials development as they combine a nanodimensional, well-defined geometry (given by their molecular nature) with the structural and chemical properties of both inorganic siliceous materials and organic molecules. The stoichiometry of these compounds shows each silicon atom bonded to one-and-a-half oxygens (sesqui-) and to a hydrocarbon (-ane), which leads to ($RSiO_{1.5}$) units.[1–3] Besides fully condensed polyhedral silsesquioxanes, which are essentially centred on cubic $R_8Si_8O_{12}$ molecules, open-corner POSS compounds with incompletely condensed silanol groups [with general formula $R_7Si_7O_9(OH)_3$], which can generally be obtained by direct synthesis from specific chlorosilanes[1–5] or by cleavage of completely condensed POSS,[6–7] are far more interesting due to the possibility of further functionalisation both with specific organosilanes and with heteroelements. In particular, these compounds (Figure 1) are suitable for reaction with a variety of transition metal complexes (in the form of alkoxides or chlorides) to form completely condensed metal-silsesquioxanes (M-POSS).[8–12] These metal-containing cage structures have proved to be promising both as homogeneous catalysts and as precursors for highly efficient metal-based heterogeneous catalysts.[13–16]

Since a wide variety of organic groups can be bound to the silicon, the inorganic cage can also show a tunable chemical affinity towards several organic solvents and also for polymeric matrices. Thus, these inorganic–organic hybrid molecular materials may be made chemically compatible towards polymers and become suitable for preparing nanocomposites. The use of cubic silsesquioxanes in the

---

[a] Dipartimento di Scienze e Tecnologie Avanzate, Interdisciplinary Center Nano-Sistemi, Università del Piemonte Orientale, INSTM Local Research Unit,
Via V. Bellini 25G, 15100 Alessandria, Italy
E-mail: enrico.boccaleri@mfn.unipmn.it
[b] Centro di Cultura per l'Ingegneria delle Materie Plastiche – Politecnico di Torino, INSTM Local Research Unit,
V.le T. Michel 5, 15100 Alessandria, Italy

[†] This young chemist died recently at the age of 34. Most of us have known him as a student or as a study companion and feel glad to honour his memory in this work.

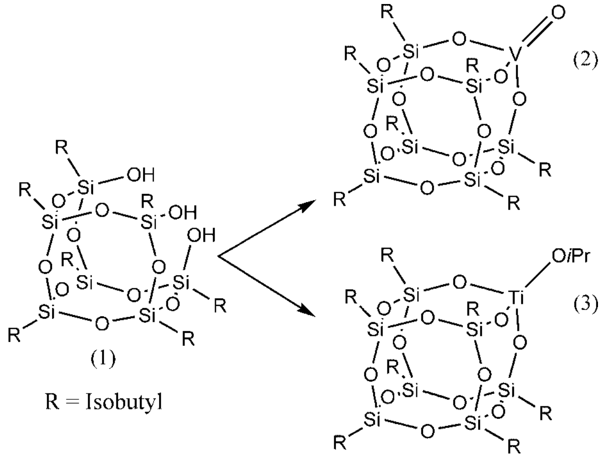

Figure 1. Trisilanolisobutyl-POSS (**1**), V-isobutyl-POSS (V-POSS; **2**) and Ti-isobutyl-POSS (Ti-POSS; 3); dimeric forms (see Figure 3 for instance) can also be present.

preparation of polymer nanocomposites has resulted in physicochemical properties that are significantly different to those of the parent polymer.[17–20] For this reason, the ability to disperse homogeneous metal-containing silsesquioxanes in polymeric matrices can lead to the distribution of well-exposed, coordinatively defined metallic centres within the organic matrix which, by acting as condensed-phase catalytic centres, can further modify the chemical behaviour of polymers, in particular at high temperatures (i.e. combustion conditions). In particular, M-POSS can deliver important flame retarding properties as they are able to activate, for instance, oxidative dehydrogenation reactions, thus reducing polymer ablation by the formation of carbonaceous and ceramic layers (given by the silica cage) on the polymer surface. Fina et al., for example, have recently shown that Al- and Zn-isobutyl-POSS are catalytic promoters of the formation of charring products during thermal oxidation of polypropylene.[21,22] Hence, interesting results can be expected when catalytically active transition metals are inserted in the siliceous cage and dispersed.

Some papers in the literature show the use of metal oxide species as additives for polymeric matrices different from polypropylene.[23] In particular, composites containing TiO_2 particles dispersed in poly(methyl methacrylate) or polystyrene have been investigated.[24–26] When reported, the presence of this inorganic filler showed interesting effects on the thermal stability of composites (for instance in the study of oxidative thermal degradation with TGA), giving a temperature shift on oxidative thermal degradation of about 50 °C for PMMA with 5–20 wt.-% of TiO_2. However, the net amount of transition metal inserted and the type of dispersion and interfacial interactions occurring with the polymer are extremely different and hard to relate to the selected M-POSS. Furthermore, as reported previously,[17–20] the introduction of silsesquioxane nanostructures can also modify other properties of the polymeric materials (i.e. mechanical behaviour).

This work focuses on the synthesis of V and Ti isobutylsilsesquioxanes by corner-capping reactions.[27–29] The synthetic conditions for the insertion of $[(n\text{PrO})_3\text{VO}]$ and $[\text{Ti}(\text{O}i\text{Pr})_4]$ within the cage of isobutyl-POSS have been optimised (solvent, temperature and reaction time) and followed by FTIR spectroscopy. The products have been thoroughly characterised by ^{29}Si{^{1}H} NMR, FTIR, FT-Raman and UV/Vis spectroscopy. The materials obtained, together with the unmodified parent silsesquioxane, have been blended with polypropylene (to the best of our knowledge, the preparation of these composites is reported here for the first time) and the composites have been characterised by thermogravimetric analysis (TGA) under nitrogen and air in order to investigate the role of the dispersed metal during thermal and thermo-oxidative degradation.

Results and Discussion

The occurrence of the corner-capping reaction of the open cage silsesquioxane was observed in the ^{29}Si{^{1}H} NMR spectra. The products were diluted with the appropriate deuterated solvents at about 5 wt.-% concentration. For example, sample **1** (Figure 2, A) gave a ^{29}Si{^{1}H} NMR spectrum (in C_6D_6 at 25 °C) that contains three distinct multiplet signals at δ = –58, –66.5 and –68 ppm in a 3:1:3 ratio. After functionalisation with a metal centre [part B of Figure 2, shows the ^{29}Si{^{1}H} NMR spectrum of V-isobutyl-POSS], the changes in the NMR spectrum are clear. Thus, the signal at δ = –58 ppm due to Si–OH is substituted by a

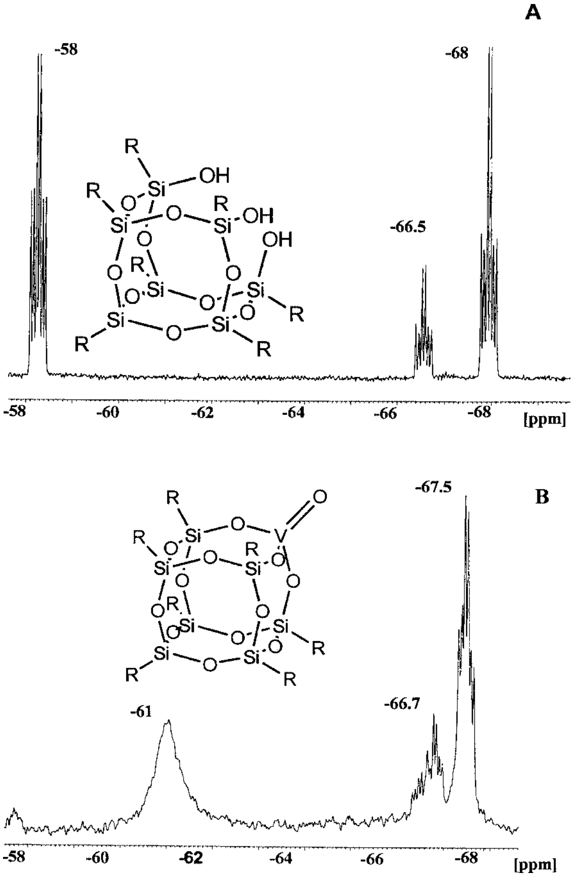

Figure 2. ^{29}Si{^{1}H}NMR spectra of **1** (A) and **2** (B).

broader signal at δ = –61 ppm in the V-containing silsesquioxane and, as expected, the fine structure of the multiplet signal disappears due to the presence of dipolar interactions with the ^{51}V nucleus. This result strongly supports the introduction of a tricoordinate vanadyl group into the cage corner of the trisilanolisobutyl-POSS, and that this is the main product. Moreover, these signals are typical of a monomeric structure of V-isobutyl-POSS, although possible changes of solution concentration and temperature can favour a dimer structure in equilibrium with the monomeric one.[28]

The Si–OH signal is also absent in the ^{29}Si{^{1}H} NMR spectrum of the titanium derivative **3**, thus suggesting that the corner-capping reaction is also successful for this compound. However, the spectrum shows a complex multiplet centred at around δ = –66.5 ppm, which was attributed to the presence of an equilibrium between dimeric and monomeric Ti-isobutyl-POSS molecules (Figure 3). This assignment was suggested by the fact that similar results have been reported for Ti-cyclohexyl-POSS.[27]

In order to evaluate the reaction evolution, and to optimise the synthesis time of V-isobutyl-POSS, the process was followed by IR spectroscopy (Figure 4A) in the liquid phase by collecting small amounts of the reaction medium. The IR spectra collected at increasing reaction time show a rapid disappearance of the broad absorption in the 3400–3100 cm^{-1} range that is attributable to the O–H stretching of H-bonded silanols of the POSS cage. The maximum of this absorption could not be detected due to overlap with the C–H stretching modes of the aromatic ring of the solvent. However, it is very clear that this absorption disappears almost completely within five minutes.

The reaction times are longer for the synthesis of Ti-isobutyl-POSS, and 90 minutes are necessary to the complete corner-capping reaction of partially condensed isobutyl-POSS (Figure 4B).

The IR spectra of M-POSS in KBr pellets (Figure 5) show a clear similarity to that of the parent open-cage POSS in the fingerprint region (1500 and 1000 cm^{-1}), where the stretching and bending modes of the isobutyl chains and of the cage framework [ν_{as}(Si–O–Si) around 1100 cm^{-1}] absorb. However, only the parent trisilanolisobutyl-POSS (**1**) shows a clear band at 890 cm^{-1} (Figure 5, curve 1) due to the bending mode of the Si–O–H groups, which is replaced by bands at 910 and 920 cm^{-1} in the case of V- and Ti-POSS respectively (Figure 5, curves 2 and 3). These absorptions, which appear with the disappearance of the Si–OH bending mode[27] of **1**, can be assigned to ν_{as}(Si–O–V)[30] and ν_{as}(Si–O–Ti),[31] respectively.

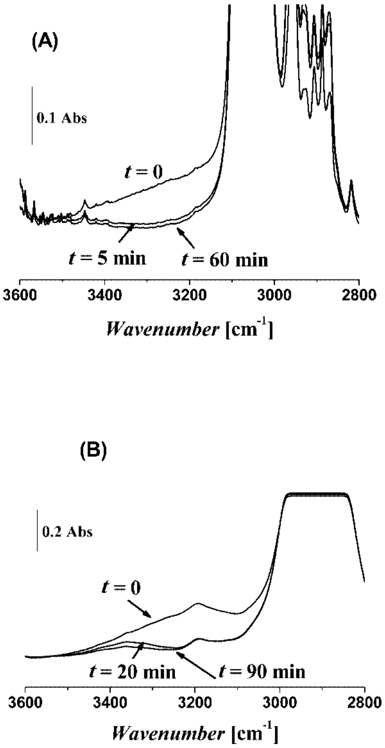

Figure 4. (A) IR spectra of the reaction mixture (in C_6H_6 solution) for the preparation of V-isobutyl-POSS; (B) IR spectra of the reaction mixture (in *n*-hexane solution) for the preparation of Ti-isobutyl-POSS.

Raman spectroscopy (Figure 6) confirmed that the vanadyl group is present in V-POSS. In fact, a sharp new peak at 1020 cm^{-1}, due to the V=O stretching vibration, is found in the Raman spectrum of V-POSS. The remaining part of the spectrum is almost unchanged with respect to the parent trisilanolisobutyl-POSS **1**. The NMR, FTIR and Ra-

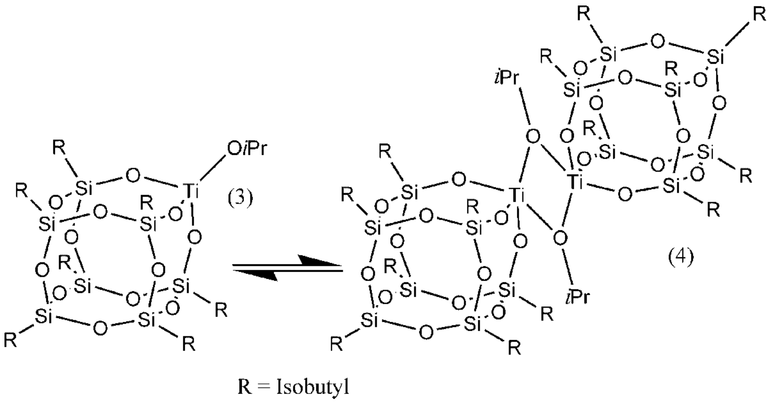

Figure 3. Schematic representation of monomeric **3** and dimeric Ti-isobutyl-POSS (**4**).

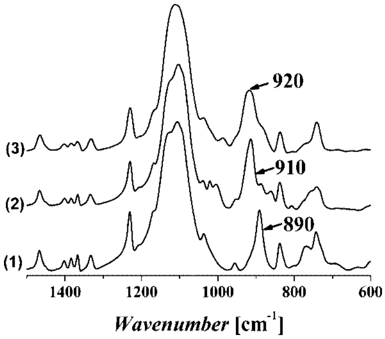

Figure 5. IR spectra (KBr pellet) of **1**–**3**.

man spectra therefore provide clear evidence that silanol groups are complexed with Ti or V metal centres leading to the closure of the isobutyl-POSS polyhedral cage.

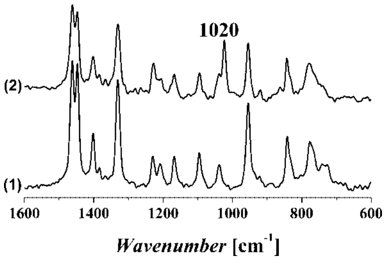

Figure 6. Raman spectra of **1** and **2**.

Diffuse-reflectance UV/Vis spectroscopy was used to monitor the oxidation states of the metals in **2** and **3**. Two bands at 250 and 300 nm are found in the spectrum of V-isobutyl-POSS (Figure 7, dotted line). These bands are assigned to low-energy charge-transfer (CT) transitions associated with framework vanadium species in a tetrahedral coordination environment.[32] In particular, the absorption at 250 nm is correlated to an electron-transfer transition between the bridging oxygens and the metal centre, while the band at 300 nm is an n → π* transition due to the terminal V=O bond.

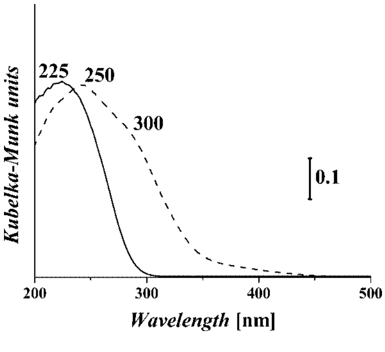

Figure 7. Diffuse reflectance UV/Vis spectra of **2** (dotted line) and **3** (solid line) mixed with anhydrous $BaSO_4$.

The vanadium centre within this material is sensitive to the presence of water, undergoing expansion of its coordination number in the presence of humidity. This was proved by recording the UV/Vis spectrum of V-isobutyl-POSS mixed with hydrated KBr. The band at 400 nm confirms a change of coordination of the metal centre, which passes from tetrahedral to fivefold coordination. It should be noted, however, that under these conditions the formation of oxide aggregation by-products is not observed. On the basis of these observations, the M-POSS complexes were stored under nitrogen in order to prevent any interaction with water.

The diffuse-reflectance UV/Vis spectrum of Ti-isobutyl-POSS (Figure 7, solid line) is characterised by a broad band at 225 nm, which is typical of tetrahedrally coordinated Ti^{IV}, as reported in the literature for similar samples[33] and mesoporous titanosilicates.[34]

Polypropylene/M-POSS Nanocomposites: Thermogravimetric Analysis

Thermogravimetry is a well-established technique for the assessment of the ability of nanoadditives to favour the activation of degradation pathways suitable to protect the polymeric matrix and delay its weight loss upon heating.[35–37] In particular, the comparative analysis of the thermal behaviour of pure polymer and nanocomposite under inert or oxidative conditions is straightforward. On the other hand, these materials may activate catalytic reactions in the condensed phase due to the presence of peculiar surface and interfacial properties, such as surface acidity or redox catalytic sites, when in contact with oxygen at a given temperature. In particular, besides oxidative phenomena (which lead to the formation of small volatile molecules or CO, CO_2 and water), oxidative dehydrogenation reactions (ODH), which can be responsible for the formation of carbonaceous products, may occur. Moreover, the inorganic fillers can provide a physical protection to the polymeric matrix by limiting the oxygen diffusion, and thus the oxidation processes, by the formation of thermally stable siliceous or carbosiliceous surface layers (physical effect).

Due to the high affinity of isobutyl-POSS for polypropylene,[38] the prepared M-isobutyl-POSS complexes were dispersed in a polypropylene matrix by melt blending to give inorganic–organic nanocomposite materials. During the preparation of composite materials in a microextruder, the extrusion process was performed in the absence of humidity at 190 °C in order to avoid possible interactions between the metal centres and the water molecules. On the basis of the results of the NMR spectra collected on solutions (discussed above) in which the concentration of M-isobutyl-POSS is higher than in the composites, assuming a similar efficient dispersion of the nanofiller within the polymeric organic matrix, it can reasonably be expected that a large amount of M-POSS within PP exists as the monomeric species. The polymer was also blended with open cage trisilanolisobutyl-POSS (i.e. without metals in the siliceous cages), following the same procedure, for comparison. This proved to be helpful to discriminate the physical and chemical role of the dispersed nanofillers (e.g. the role of metal centres in promoting ODH reactions).

TGA measurements run under nitrogen showed that the maximum decomposition rate of pure polypropylene (Figure 8, curve A) occurs at about 454 °C (see the weight loss derivative curves, DTG, in the bottom panel). The addition of trisilanolisobutyl-POSS (Figure 8, B) and Ti-isobutyl-POSS (Figure 8, D) does not significantly change the thermal behaviour of the polypropylene, whereas in the presence of V-isobutyl-POSS (Figure 8, C) the degradation occurs at slightly higher temperature (464 °C).

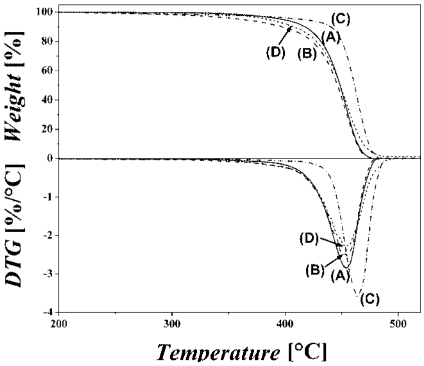

Figure 8. TGA measurements (10 °C min^{-1}) under nitrogen (the derivative curves, DTG, are shown in the bottom panel) for PP (A), PP-trisilanolisobutyl-POSS (3 wt.-%; B), PP-V-isobutyl-POSS (3 wt.-%; C) and PP-Ti-isobutyl-POSS (3 wt.-%; D).

On the other hand, large modifications of the thermal degradation behaviour were observed with both Ti- and V-isobutyl-POSS when heating the composites in air (Figure 9). In an oxidative atmosphere, the thermal oxidation of pure polypropylene occurs with maximum rate (measured from the DTG curve) at 327 °C (Figure 9, A) and the presence of trisilanolisobutyl-POSS (Figure 9, B) has only a limited effect, shifting the maximum weight loss rate to 335 °C. The effect of the presence of V-isobutyl-POSS (Figure 9, C) and Ti-isobutyl-POSS (Figure 9, D) is well evident from curves C and D in Figure 9, where a significant shift of the whole thermal oxidation process towards higher temperature can be observed. In detail, the degradation onset temperature (calculated when the decomposition reaches 5% of weight loss) for composites with M-isobutyl-POSS, reported in Table 1, are shifted to 290 and 303 °C, respectively, an increase of 43 and 56 °C with respect to pure polypropylene (onset temperature: 247 °C). The temperatures of maximum decomposition rate (by DTG profiles), which were found to be 327 °C for the pristine PP matrix, 390 °C for the PP-Ti-isobutyl-POSS composite and 375 °C for the PP-V-isobutyl-POSS composite, further confirmed this evidence. This effect can be attributed to the presence of Ti and V catalytic centres, which are active in ODH reactions and promote the formation of thermally stable char products. This is demonstrated by the presence of a meaningful amount of degradation products, which are oxidised only at temperatures higher than 400 °C. Indeed, while the residues of polypropylene and the PP-trisilanolisobutyl-POSS composite oxidised above 400 °C are very low, a far greater amount (about 20 wt.-%) can be detected with M-isobutyl-POSS (in particular Ti-isobutyl-POSS; Table 1).

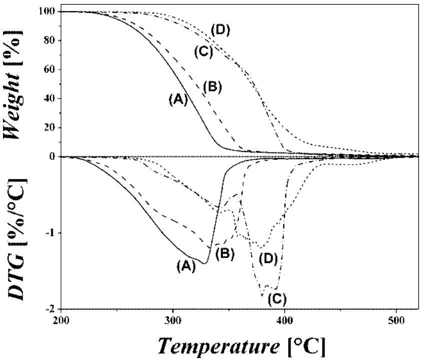

Figure 9. TGA measurements (10 °C min^{-1}) under air (the derivative curves, DTG, are shown in the bottom panel) for PP (A), PP-trisilanolisobutyl-POSS (3 wt.-%; B), PP-V-isobutyl-POSS (3 wt.-%; C) and PP-Ti-isobutyl-POSS (3 wt.-%; D).

Table 1. Comparison of the degradation processes of PP, PP-trisilanolisobutyl-POSS and PP-M-isobutyl-POSS composites from TGA data under oxidative conditions.

	T_{onset} [°C]	T_{max} [°C]	Residue at 400 °C
Polypropylene (PP)	247	327	2.5%
PP-trisilanolisobutyl-POSS	255	335	2.5%
PP-V-isobutyl-POSS	290	390	6%
PP-Ti-isobutyl-POSS	303	375	20%

Further evidence for the role of M-POSS on the oxidative thermal degradation of the polymeric matrix can be found by monitoring the weight loss under isothermal conditions in air (Figure 10). When setting the temperature to the beginning of the degradation of the pure matrix (i.e. 250 °C), neat PP and trisilanolisobutyl-POSS showed a very similar behaviour, with a rapid degradation that led to a residue of around 10 wt.-% in only 50 min (Figure 10, curves A and B). On the contrary, polypropylene composites containing both V- and Ti-isobutyl-POSS showed a massive formation of thermally stable products. After 250 min, in fact, residues of 28 and 42 wt.-% were found for V-isobutyl-POSS (Figure 10, C) and Ti-isobutyl-POSS (Figure 10, D), respectively. These results can be explained by the presence of catalytically active metal centres dispersed within the polymeric matrix, which result in the formation of thermally stable charring products, and suggest that the phenomenon is sensitive to the chemical nature of the metal centres.

The μ-ATR-IR spectroscopic data of composites containing Ti- and V-isobutyl-POSS were recorded on the residues at 250 °C. As shown in Figure 11, the presence of a band at 1600 cm^{-1} suggests that the metal-containing nanofillers activate the early formation of unsaturated moieties as degradation products of the polypropylene matrix in the presence of oxygen. The bands observed at 1770 and 1710 cm^{-1} can be attributed to the formation of oxidised species (i.e. γ-lactones and ketones).[39] The formation of extended conjugated unsaturated regions, which is favoured by the catalytic role of the metal centres, could be responsible for the stabilization of the thermal behaviour of the polymer, in agreement with the thermogravimetric analysis.

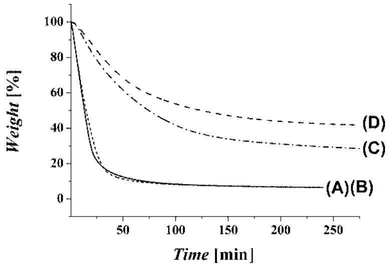

Figure 10. TGA measurements under isothermal conditions (250 °C) in air for PP (3 wt.-%; A), PP-trisilanolisobutyl-POSS (3 wt.-%; dotted line, B), PP-V-isobutyl-POSS (3 wt.-%; C) and PP-Ti-isobutyl-POSS (3 wt.-%; D).

Further studies on the mechanism acting within the M-POSS polypropylene composites carried out with several spectroscopic techniques highlight and confirm the solid-state catalytic activity of the nanofillers within the polymeric matrix.[40]

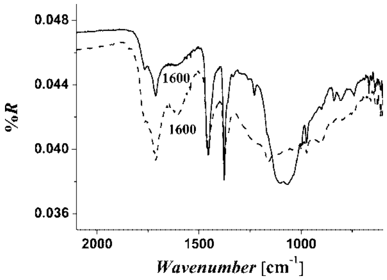

Figure 11. µ-ATR-IR spectra of the residues obtained at 250 °C under air flow for PP-Ti-isobutyl-POSS (solid line) and PP-V-isobutyl-POSS (dashed line).

When polypropylene is blended with Ti-POSS, the stabilisation effect on the polymer is more effective. These results are far more remarkable when the extremely low amount of metal dispersed in the material is considered (less than 0.2 wt.-%).

Conclusions

This article focuses on the synthesis of V- and Ti-functionalised cubic silsesquioxanes, which are reported for the first time with an isobutyl substituent on the cage corners. A detailed characterisation during the synthetic procedure has highlighted that the reaction times are very short with respect to the results published on POSS with different organic substituents. Besides solution $^{29}Si\{^1H\}$ NMR, FTIR spectroscopy is a sensitive probe for the monitoring of the corner-capping reaction and the characterisation of the products, while Raman spectroscopy can often provide complementary information about the nature of the transition metal centres inserted into the cage. The coordination state of the metallic centres has been investigated by diffuse reflectance UV/Vis spectroscopy.

Due to their chemical affinity, these compounds have been used as additives (3 wt.-%) in polypropylene by melt blending to give nanocomposite materials. The thermal degradation of these materials under an inert or oxidative atmosphere was followed by thermogravimetric analysis. Whilst metal-free additives (i.e. trisilanolisobutyl-POSS) have limited effects on the degradation pathway of the polymeric matrix, Ti-POSS and V-POSS shift the oxidative degradation significantly to higher temperature (around 70–80 °C). Moreover, under isothermal conditions, while neat polypropylene and metal-free PP-POSS composites degrade rapidly at 250 °C in air (leaving less than 10% of residue after 50 min), in the presence of V- and Ti-POSS the degradation is significantly slower and leads to large amounts of residues: 28% and 42% respectively after 250 min. This suggests that metal-bearing nanofillers can operate chemically on the polymeric matrix degradation pathway, thereby inducing significant modifications to the high temperature oxidative processes. In particular, oxidative dehydrogenation reactions, which lead to thermally stable charring products, are seemingly favoured in this case.

A more detailed multi-technique investigation, which is currently in progress, is needed to highlight the chemical reactivity induced by the presence of M-POSS and the related evolution of the species that are formed within the polymeric matrix.

Experimental Section

Materials: Trisilanolisobutyl-POSS (**1**) from Hybrid Plastics Company was used as precursor for the preparation of M-isobutyl-POSS by a corner-capping reactions. The preparation was performed under inert conditions (nitrogen). All solvents, freshly opened, were used without further purification.

V-Isobutyl-POSS (2): An equimolar solution of $[(nPrO)_3VO]$ (98%, Sigma Aldrich) and trisilanolisobutyl-POSS was prepared by adding a 2-mL solution of $[(nPrO)_3VO]$ (288 µL, 1.27×10^{-3} mol) in benzene to a solution of **1** (1.00 g, 1.27×10^{-3} mol) in 20 mL of benzene under vigorous stirring. As found by IR spectroscopy, trisilanolisobutyl-POSS was almost completely transformed within a few minutes; however, the mixture was stirred for 1.5 h to complete the reaction. Filtration through a fine sintered glass funnel, and solvent removal in vacuo, led to the isolation of 900 mg of V-isobutyl-POSS as a white amorphous foam.

Ti-Isobutyl-POSS (3): $[Ti(OiPr)_4]$ (375 µL, 1.27×10^{-3} mol; 97%, Sigma Aldrich) was added with vigorous stirring to a solution of **1** (1.00 g, 1.27×10^{-3} mol) in 160 mL of *n*-hexane. The reaction solution was carefully purged with nitrogen to prevent the rapid hydrolysis of $[Ti(OiPr)_4]$. After addition, the temperature was raised to 60 °C and the mixture stirred for 90 min. In this case, FTIR spectroscopy showed that the transformation of trisilanolisobutyl-POSS was almost complete within 1.5 h. Subsequently, the solvent was evaporated until a white powder (900 mg) was obtained.

Both complexes were stored under nitrogen in order to prevent any interaction with water.

Melt blending of M-isobutyl-POSS in a polypropylene matrix (3 wt%) was performed using a Basell Moplen HP501L Polypropylene Homopolymer (density: 0.9 g cm^{-3}). The melt flow rate (MFR) (230 °C/2.16 kg) was 6.0 g/10 min. The mixing was performed using a Haake twin screw microextruder at 190 °C for 10 min. The extruder was driven at 100 rpm.

Characterisation: $^{29}Si\{^1H\}$ NMR spectra of the samples dissolved in C_6D_6 (concentration: 0.1 M) at room temperature were recorded with a Jeol Eclipse Plus spectrometer equipped with an 8-T magnet.

Infrared (IR) spectra of solid samples in KBr pellets were recorded in the range 4000–400 cm^{-1} at 4-cm^{-1} resolution with a Bruker Equinox 55 spectrometer.

ATR spectra of the samples were recorded in the range 4000–500 cm^{-1} at 4-cm^{-1} resolution with a Perkin–Elmer Spectrum GX FTIR SystemMultiscope FTIR Microscope.

Raman spectra were recorded in the range 4000–50 cm^{-1} at 4-cm^{-1} resolution (500 scans) with a RFS 100 Bruker FT-Raman spectrometer equipped with a 1064-nm wavelength excitation laser. The laser power was set at 100 mW.

UV/Vis spectra were recorded in the range 190–750 nm with a Perkin–Elmer Lambda 900 spectrometer equipped with a diffuse reflectance sphere attachment (DR-UV/Vis). The samples were dispersed in anhydrous $BaSO_4$ (10 wt.-%).

Thermogravimetric analyses (TGA) of composite materials (M-isobutyl-POSS dispersed in polypropylene) were performed in air or nitrogen (60 mL min^{-1}) with a Q500 TA Instruments thermobalance, heating from 50 to 600 °C at 10 °C min^{-1} or under isothermal conditions, with 10-mg samples.

Acknowledgments

The authors thanks Dr. Nadia Tzankova Dintcheva of the University of Palermo for blending M-POSS in PP. The authors are grateful to the European Commission for financial support by means of the Specific Targeted Research or Innovation Project (STRP) project “Nanofire” (proposal no. 505637-1) in the context of the 6th Framework Programme. Financial support by the Ministero per l’Università e la Ricerca Scientifica (MIUR) through a PRIN 2002 project is gratefully acknowledged.

---

[1] R. H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, *Chem. Rev.* **1995**, *95*, 1409.
[2] P. G. Harrison, *J. Organomet. Chem.* **1997**, *542*, 141.
[3] P. P. Pescarmona, T. Maschmeyer, *Aust. J. Chem.* **2001**, *54*, 583.
[4] F. J. Feher, T. A. Budzichowski, R. L. Blanski, K. J. Weller, J. W. Ziller, *Organometallics* **1991**, *10*, 2526.
[5] P. A. Agaskar, *Colloids Surf.* **1992**, *63*, 131.
[6] F. J. Feher, R. Terroba, J. W. Ziller, *Chem. Commun.* **1999**, 2309.
[7] F. J. Feher, D. Soulivong, G. T. Lewis, *J. Am. Chem. Soc.* **1997**, *119*, 11323.
[8] R. W. J. M. Hanssen, R. A. van Santen, H. C. L. Abbenhuis, *Eur. J. Inorg. Chem.* **2004**, 675.
[9] F. J. Feher, J. F. Walzer, *Inorg. Chem.* **1991**, *30*, 1689.
[10] K. Wada, M. Nakashita, A. Yamamoto, T. Mitsudo, *Chem. Commun.* **1998**, 133.
[11] T. Maschmeyer, M. C. Klunduk, C. M. Martin, D. S. Shephard, J. M. Thomas, B. F. G. Johnson, *Chem. Commun.* **1997**, 1847.
[12] P. Smet, B. Devreese, F. Verpoort, T. Pauwels, I. Svoboda, S. Foro, J. Van Beeumen, L. Verdonck, *Inorg. Chem.* **1998**, *37*, 6583.
[13] H. C. L. Abbenhuis, *Chem. Eur. J.* **2000**, *6*, 25.
[14] S. Krijnen, H. C. L. Abbenhuis, R. W. J. M. Hanssen, J. H. C. van Hooff, R. A. van Santen, *Angew. Chem. Int. Ed.* **1998**, *37*, 356.
[15] N. Maxim, A. Overweg, P. J. Kooyman, J. H. M. C. van Wolput, R. W. J. M. Hanssen, R. A. van Santen, H. C. L. Abbenhuis, *J. Phys. Chem. B* **2002**, *106*, 2203.
[16] M. D. Skowronska-Ptasinska, M. L. W. Vorstenbosch, R. A. van Santen, H. C. L. Abbenhuis, *Angew. Chem. Int. Ed.* **2002**, *41*, 637.
[17] P. T. Mather, H. G. Jeon, A. Romo-Uribe, T. S. Haddad, J. D. Lichtenhan, *Macromolecules* **1999**, *32*, 1194.
[18] S. H. Phillips, T. S. Haddad, S. J. Tomczak, *Curr. Opin. Solid State Mater. Sci.* **2004**, *8*, 21.
[19] J. Pyun, K. Matyjaszewski, *Macromolecules* **2000**, *33*, 217.
[20] J. D. Lichtenhan, J. J. Schwab, W. A. Reinerth, *Chem. Innovation* **2001**, *31*, 3.
[21] A. Fina, H. C. L. Abbenhuis, D. Tabuani, A. Frache, G. Camino, *Polym. Degrad. Stab.* **2006**, *91*, 1064.
[22] A. Fina, H. C. L. Abbenhuis, D. Tabuani, G. Camino, *Polym. Degrad. Stab.* **2006**, *91*, 2275.
[23] U. Schubert, *Chem. Mater.* **2001**, *13*, 3487.
[24] A. Laachachi, E. Leroy, M. Cochez, M. Ferriol, J. M. Lopez Cuesta, *Polym. Degrad. Stab.* **2005**, *89*, 344.
[25] A. Laachachi, M. Cochez, M. Ferriol, J. M. Lopez Cuesta, E. Leroy, *Mater. Lett.* **2005**, *59*, 36.
[26] Y. Yang, P. Wang, *Polymer* **2006**, *47*, 2683.
[27] T. Maschmeyer, M. C. Klunduk, C. M. Martin, D. S. Shephard, J. M. Thomas, B. F. G. Johnson, *Chem. Commun.* **1997**, 1847.
[28] F. J. Feher, J. F. Walzer, *Inorg. Chem.* **1991**, *30*, 1689.
[29] B. A. Morrow, A. J. McFarlan, *J. Phys. Chem.* **1996**, *92*, 1395.
[30] P. R. H. P. Rao, A. V. Ramaswamy, P. Ratnasamy, *J. Catal.* **1992**, *137*, 225.
[31] C. Perego, G. Bellussi, C. Corno, M. Taramasso, F. Buonuomo, A. Esposito, *Stud. Surf. Sci. Catal.* **1986**, *28*, 129.
[32] A. Albuquerque, H. O. Pastore, L. Marchese, *Stud. Surf. Sci. Catal.* **2005**, *155*, 45.
[33] Gianotti, A. Frache, S. Coluccia, J. M. Thomas, T. Maschmeyer, L. Marchese, *J. Mol. Catal. A* **2003**, *204*, 483.
[34] E. Gianotti, V. Dellarocca, L. Marchese, G. Martra, S. Coluccia, T. Maschmeyer, *Phys. Chem. Chem. Phys.* **2002**, *4*, 6109.
[35] M. Zanetti, G. Camino, P. Reichert, R. Mülhaupt, *Macromol. Rapid Commun.* **2001**, *22*, 176.
[36] M. Zanetti, G. Camino, R. Thomann, R. Mülhaupt, *Polymer* **2001**, *42*, 4501.
[37] A. Riva, M. Zanetti, M. Braglia, G. Camino, L. Falqui, *Polym. Degrad. Stab.* **2002**, *77*, 299.
[38] A. Fina, D. Tabuani, A. Frache, G. Camino, *Polymer* **2005**, *46*, 7855.
[39] G. A. George, M. Celina, A. M. Vassallo, P. A. Cole-Clarke, *Polym. Degrad. Stab.* **1995**, *48*, 199.
[40] F. Carniato, E. Boccaleri, L. Marchese, A. Fina, D. Tabuani, G. Camino, manuscript in preparation.

Received: July 21, 2006