

# POSS-based hybrids by melt/reactive blending†

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Organic–inorganic polyhedral oligomeric silsesquioxane (POSS)–polymer hybrids have gained a wide research interest in the last decade, thanks to the great versatility of POSS synthesis and availability of different chemical structures, aimed at modifications of physical/chemical properties of polymers or at delivering new functional properties.

Traditionally, *in situ* copolymerisation of POSS to produce hybrid organic–inorganic polymers with pendent POSS groups has been used both for thermoplastics and thermosets. In recent years, attention has been also given to the possibility of preparing POSS–polymer systems by melt blending techniques, taking advantage of (i) miscibility of POSS into polymers thanks to physical interactions or (ii) chemical reaction between POSS and the polymer. These two methods, usually referred to respectively as melt blending and reactive blending, represent very appealing, inexpensive and environmentally friendly processes for industrial development of POSS technology.

This paper reviews the present state of the art on both melt blending and reactive blending of POSS into thermoplastic polymers, discussing present achievements and limitations from both methods.

## Introduction

In the past decade, researchers' interest has been widely attracted by organic–inorganic hybrid compounds, aiming at obtaining

new materials bridging the gap between organic polymers and ceramics.<sup>1–3</sup>

In this frame, significant attention has been given to silsesquioxanes, a class of organosilicon compounds with general formula (RSiO<sub>1.5</sub>)<sub>n</sub> where R is hydrogen or an organic group, such as alkyl, aryl or any of their derivatives. In silsesquioxanes, each Si atom is therefore bound on average to 1.5 oxygen atoms and to a hydrocarbon group. Many different silsesquioxane structures have been prepared, with different degrees of symmetry, including random, ladder, polyhedral or mixed structures and incompletely condensed polyhedra.<sup>4–7</sup>

Polyhedral oligomeric silsesquioxanes (POSS), are the most widely studied silsesquioxanes, due to the coupling of properties

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from the thermally and chemically robust inorganic Si–O core and the organic functionalisation, allowing tailoring of compatibility and reactivity with polymers. POSS, also referred to as molecular silica, can be used to modify the properties of organic polymers, acting at the molecular level owing to their size (approx. 1 to 3 nm) comparable to polymer segments and coils. Moreover, the tailorable and perfectly defined structure makes POSS versatile nano-building blocks in the preparation of organic–inorganic hybrid materials. Several different polyhedral structures may be obtained tailoring the synthesis conditions, among which cubic cages ( $T_8$ ), are by far the most common.

From a general point of view, the addition of POSS to organic polymers was found to drastically modify the polymer's thermal properties supplying improved thermal stability as well as modifying the polymer glass transition temperature, stiffness and resilience. Moreover, incorporation of POSS molecules was responsible for reductions in the rate of combustion in the event of fire, improved dielectrical properties as well as for bringing other functional properties, accordingly with the high versatility of POSS synthesis.

While incorporation of POSS by copolymerisation with styryl-based monomers, acrylates, olefins and thermosets is well known,<sup>8,9</sup> preparation of polymer–POSS systems by solution blending or melt blending has attracted significant research efforts only in recent years.<sup>10,11</sup>

This paper is intended to give an updated review of incorporation of POSS into thermoplastic polymers by melt blending processes, both regarding dispersion driven by physical interactions (melt blending) or by chemical reactions in the molten state (melt reactive blending).

## Results and discussion

### Melt blending

The challenge of obtaining precise control of nanoscale structures in polymers by conventional processing methods used for polymer compounds and traditional microcomposites has attracted great attention since the 90s. As a result, methods to

prepare polymer nanocomposites by melt extrusion were successfully developed for various nanoparticles, such as nanoclays,<sup>12–15</sup> carbon nanotubes<sup>16,17</sup> and various metal oxides and hydroxides.<sup>18,19</sup>

Compared to *in situ* polymerisation methods, melt blending presents several advantages, being an inexpensive, fast and versatile technology. Indeed, standard equipment used for polymer compounding, such as twin screw extruders, are generally suitable for the processing of nanostructured polymers, with limited modifications. Extrusion is usually a very fast method, having blending times of the order of minutes, so that high throughput is possible with relatively small equipment. Moreover, no organic solvents are generally used during melt blending, which results in a relatively low environmental impact. However, successful nanocomposite melt blending requires very careful design of the processing conditions to obtain a proper dispersion and distribution of nanoparticles. Variables to be optimised include equipment parameters such as temperature, time, shear forces as well as the choice of proper compatibilising agents and nanoparticle functionalisation. Furthermore, online characterisation of material properties during processing is in its infancy and needs significant developments to attain a strict control of nanostructured materials.

In preparation of polymer–POSS by melt blending, the key point is the chemical–physical interaction between POSS and the matrix. The unique feature of POSS having a precisely controlled chemical structure with tailorable organic groups covalently attached to the Si–O framework allows in principle to obtain tunable miscibility into organic polymers. However, strong self-interaction between geometrically regular POSS cages often results in POSS aggregation, which has to be carefully taken into account when aiming at POSS molecular dispersion into polymers.

A review of the results obtained by melt blending of POSS in the main polymer groups is given in this section. Focus is given to the dispersion level obtained and, whenever possible, on the correlations between POSS dispersion and properties obtained.

Fine POSS dispersion has to be necessarily pursued, because proper exploitation of POSS properties is only obtained when POSS is dispersed at molecular level or in nanosized clusters. Indeed, aggregation of POSS into microparticles does not allow one to take advantage of the intrinsic POSS features and would result in properties which can be obtained with microparticles, thus making the use of POSS unjustified, because of their higher cost.

**Polyolefines.** Polyolefines are certainly the polymer class in which POSS incorporation by melt blending has been so far most studied.

Fu *et al.*<sup>20</sup> reported the first study concerning polypropylene (PP)–octamethyl POSS composites obtained by melt blending in an internal mixer, evaluating their crystallisation behaviour under quiescent and shear states, whereas no characterisation of POSS dispersion was reported. In quiescent conditions, POSS was found to enhance crystallization rate, attributed to nucleation on crystals of aggregated POSS, with maximum nucleation efficiency at POSS loadings of about 15% wt. However, at 30% wt. POSS loading retarded crystallization was observed and attributed to dispersed POSS molecules reducing the mobility of



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PP chains. On the other hand, POSS always accelerated crystallisation under shear; an explanation was proposed based on physical crosslinking action of POSS when shear is imposed, thus increasing the relaxation time and creating a higher population of nuclei.

Very similar results were reported by Chen *et al.*, showing that the crystallization rate of PP increased with the increase in octamethyl POSS contents (1 to 10% wt.) during crystallization.<sup>21</sup> Such behaviour was explained by the POSS aggregation forming nanocrystals and acting as an effective nucleating agent for PP. In a later paper,<sup>22</sup> Chen *et al.* observed that in addition to the nucleation effect of octamethyl POSS nanocrystals, a minor molecularly dispersed POSS amount resulted in retarded nucleation and growth rates.

Ethylene-propylene (EP) copolymer–octamethyl POSS nanocomposites were prepared by melt-mixing with EP copolymers characterised by different ethylene contents and varying the POSS loadings from 10 to 30% wt.<sup>23</sup> From XRD analysis it was found that no molecular dispersion of POSS cages could be achieved as the POSS X-ray pattern was maintained in the composites. Small-amplitude oscillatory shear experiments showed that the presence of POSS molecules changed the rheological behaviour above melting from liquid-like in the neat resin to solid-like in the nanocomposites. Moreover, the addition of 10% wt. of POSS was found to increase considerably the elastic modulus (about 70%) in all the temperature range from  $-80$  to  $+60$  °C as well as to shift the glass transition temperature ( $T_g$ ) to higher temperature (by about 5 °C), compared to neat EP.

The non-isothermal crystallisation of high density polyethylene (HDPE)–octamethyl POSS nanocomposites, with POSS loading ranging from 1 to 10% wt., was studied by Joshi *et al.*, but no characterisation of POSS dispersion was reported.<sup>24</sup> POSS exhibited nucleation activity only at 10% wt. loading in HDPE and was not an effective nucleant at lower loadings. In a later paper, the same authors extended the investigation to isothermal crystallisation of HDPE–octamethyl POSS, observing that crystallization half-time decreases for all nanocomposites when compared with neat HDPE and it is minimal for 1% wt. POSS loading, explained by the finer dispersion of POSS obtained at a low concentration. The authors claimed that only the POSS dispersed at the molecular level affects the rate of crystallization of the HDPE matrix under isothermal crystallization conditions by acting as a heterogeneous nucleating agent.<sup>25</sup> However, this appears contradictory, since heterogeneous nucleation implies the presence of a heterogeneity over which the polymer is nucleated, whereas molecular dispersion of POSS means solubility in the polymer matrix to obtain a single phase. In the same HDPE–POSS blends, octamethyl POSS was shown to act as a lubricant at low concentrations (0.25 and 0.5% wt.), while at higher concentrations chain mobility is hindered and viscosity increases. Above 5% wt. POSS in HDPE, solidlike behavior at low shear rate is observed. However, the strength of this network is poor and easy to break under moderate shear forces.<sup>26</sup> Attempts to prepare linear low density polyethylene–octamethyl POSS nanocomposites were reported by Hato *et al.*,<sup>27</sup> showing extensive microaggregation, despite the lower crystallinity of linear low density polyethylene (LLDPE) which was expected to provide more free volume to host POSS molecules, compared to HDPE.

The effect of different side groups on POSS was first studied in polypropylene, by melt blending with POSS carrying different alkyl R substituents and different POSS loadings.<sup>28</sup> Substantial differences have been found in the morphology of the composites by increasing the alkyl chain length from octamethyl POSS to octaisobutyl POSS. When loading at 3% wt., the compatibility between methyl POSS and PP is very low and the filler is distributed within the matrix in micronic aggregates. On the other hand, the isobutyl substituents determined a submicronic dispersion, as determined by SEM imaging; a further increase in the substituent chain length to octyl does not bring any apparent improvement on POSS dispersion. This evidenced that POSS dispersion into the organic matrix is driven by the chemical interactions between PP chains and organic groups on POSS. When R = methyl, a weak interaction polymer–POSS takes place and POSS aggregation is favoured, due to attractive forces between polarities on Si–O cores. Conversely, longer alkyl chains give stronger interactions with PP and reduce the POSS cohesive force, resulting in a higher compatibility. When increasing the POSS loading to 10% wt., the morphology for PP–methyl POSS is very similar to that observed at lower concentration, except for the higher number of POSS aggregates. Interestingly, at 10% wt. loading, POSS aggregates are also observable with R = isobutyl, suggesting the overcoming of a solubility limit. On the other end, PP–10% octyl POSS still does not show any micron size aggregates. The crystallization and melting behaviour of the same PP–POSS composites with different alkyl substituents and different POSS loadings was also investigated.<sup>29</sup> The crystallization kinetics of the composites from the melt, examined both in isothermal and non-isothermal conditions, demonstrated that the activity of the examined POSS in the crystallisation process is related to the length of alkyl substituents, which affect the filler dispersion in the PP matrix. While octamethyl POSS turned out to be a nucleating agent for PP at all explored compositions and cooling conditions, octaisooctyl POSS retarded the crystallization kinetics, likely due to the high dispersion of this filler which hinders macromolecular movements, thus resulting in a reduced growth rate. Octaisobutyl POSS showed a different behaviour depending on the loading amount in PP: at low content (3% wt.) the POSS nano-dispersion hinders the PP crystal growth, thus resulting in a retarded crystallization; at higher content (10% wt.) this effect is counterbalanced by the presence of octaisobutyl POSS crystals, which behave as nucleants for PP.

The type of alkyl substituents on POSS also affects mechanical properties: tensile tests showed that the incorporation of octamethyl POSS induces an increase in Young's modulus and a reduction of the yield strength in comparison with unfilled PP. By contrast, upon the incorporation of octaisobutyl POSS and isooctyl POSS, both Young's modulus and the yield strength were found to decrease by increasing the POSS content. It was suggested that POSS behave as particles having a siliceous hard-core surrounded by a hydrocarbon soft-shell, which limits the stress transfer from the matrix to the core in dependence on the length of the alkyl groups.<sup>30</sup>

Dielectrical properties of PP–POSS blends with either octamethyl POSS or octaisooctyl POSS were reported; results of the relative permittivity, loss factor and volume resistivity measurements indicated that octamethyl POSS could have an effect on the dielectric properties of PP, assumed to be related to charge



scavenging by POSS segregated on the boundaries between spherulites, whereas isooctyl POSS did not significantly affect dielectrical properties.<sup>31</sup>

Surface properties of octaisobutyl POSS–PP, prepared at variable POSS concentrations *via* melt blending, were also addressed.<sup>32</sup> Ultra-low friction and enhanced hardness, modulus, and hydrophobicity were observed for the nanocomposite surfaces, with minimal changes in the bulk thermomechanical properties, due to significant differences in POSS distribution and aggregation in the surface and the bulk, with preferential segregation of POSS to the surface. The migration process of POSS to the surface of POSS-nanocomposites was found to be very significant especially after annealing treatment. Migration mechanisms were studied in detail and different reasons for POSS migration was suggested, namely related to its lower surface tension, the entropy considerations and its lower cohesive energy with the matrix chains as compared to the cohesion energy between the chains.<sup>33</sup>

From the above reviewed results, obtaining a molecular dispersion of POSS into semicrystalline polyolefines appears to be very challenging, especially with POSS carrying small alkyl substituents and at relatively high loadings. This is attributed, on one hand, to the high crystallinity of polyolefins, which leave relatively little volume to POSS bulky molecules, which can be easily hosted in the amorphous phase only. On the other hand, POSS with short alkyl chains generally show high crystallinity and higher melting points compared with longer chains,<sup>34</sup> evidencing stronger self-interactions.

The problem of POSS aggregation into polymers was addressed by means of computational modelling. The influence of blending polyhedral oligomeric silsesquioxane substituted with cyclopentyl rings into a polyethylene matrix was probed using atomistic simulations, with POSS loadings ranging from 5 to 25% wt. Interactions between POSS particles were found to promote organization of POSS within the polymer, where clear signs of aggregation were observed.<sup>35</sup> Very recently, Zeng *et al.* reported molecular simulation of six different polyvinylidene fluoride (PVDF)/POSS mixtures, with POSS carrying ethyl, phenyl, trifluoropropyl or longer fluorinated linear chains as organic substituents.<sup>36</sup> Results indicate that fluorinated POSS is fully miscible in PVDF at any temperature, whereas ethyl and phenyl POSS are immiscible, due to the lack of strong electrostatic interactions between non-fluorinated POSS and the PVDF matrix.

The comparison between dispersions obtained with polysilsesquioxanes carrying the same organic substituents but having different geometrical structures evidences how important the self-interactions between polysilsesquioxanes are in determining the final dispersion into the polymer matrix. Octavinyl  $T_8$  POSS and vinyl polysilsesquioxane with a cage/ladder mixed structure were blended into PP in the same conditions and at the same silsesquioxane loading, showing significant differences.<sup>37</sup> In the first case micron-size POSS aggregates were observed, similarly to the case of octamethyl POSS previously described; on the opposite, no clustering is observable for the mixed cage/ladder structure and the morphology appears to be homogeneous at the submicronic scale.<sup>38</sup> Provided that the chemical interaction of both vinyl polysilsesquioxanes with PP is similar, the differences in silsesquioxane dispersion must be due to the different cohesion

of molecules of the two silsesquioxane species. In fact, the regular  $T_8$  structure allows systematic interactions between adjacent cages, leading to packing of POSS into a crystalline structure which is stable up to temperatures higher than that for PP blending, whereas the vinyl polysilsesquioxane with cage/ladder mixed structure is a liquid at room temperature.

**Vinyl polymers.** The preparation of polymethylmethacrylate (PMMA)–POSS nanocomposites by melt blending was studied, in comparison with corresponding copolymers, evidencing low POSS solubility and formation of crystallites in addition to a limited nanodispersed fraction.<sup>39</sup> Octacyclohexyl POSS and octaisobutyl POSS were blended with a PMMA homopolymer; at low loadings ( $\leq 5\%$  vol.), a significant fraction of POSS resides in the matrix in a nanoscopically dispersed state. Above this concentration, an apparent solubility limit is reached, beyond which additional untethered POSS aggregates into crystallites in the PMMA matrix, increasing the viscosity of the polymer in a way analogous to hard spheres. Octaisobutyl POSS was also blended into a poly(methyl methacrylate-*co*-propyl methacrylate isobutyl POSS) to evaluate the interaction of untethered POSS with polymer chains carrying POSS chemically bound as pendent moieties. The copolymer blends showed lower crystalline aggregation of untethered POSS and a substantial increase in viscosity at all loadings, attributed to a substantial retardation of chain relaxation processes caused by significant association between the POSS cages on the chains and those in the blend.<sup>39</sup> Recently reported molecular dynamic simulations of PMMA–POSS<sup>40</sup> are in good agreement with experimental results described above, suggesting that homogeneous dispersion of octaisobutyl POSS is obtainable below 15% wt. loading, whereas above 20% wt. loading, POSS molecules aggregate into crystallites.

Melt-mixed blends of PMMA with acrylic POSS showing miscibility up to 10% vol. were also reported.<sup>41</sup> Well-dispersed POSS showed a clear plasticising effect, due to an increase in the free volume within the PMMA matrix, thus lowering the  $T_g$  (*e.g.* by about 5 °C and 11 °C when loading 5% vol. or 20% vol. octa-acrylic POSS, respectively) and decreasing the melt-state viscoelastic modulus. Deep investigation of the POSS effect on free volume when mixing in PMMA was also reported for oligomeric PMMA–octamethacryloxypropyl POSS as a model system.<sup>42</sup>

Octa(tetramethylammonium) POSS was blended with PS, aiming at decreasing flammability and improving thermal properties. While loadings  $\leq 5\%$  wt. POSS clusters of about 100 nm or less are found, a very peculiar nanofibre-like aggregation is obtained for POSS loadings  $\geq 20\%$  wt., attributed to strong electrostatic interactions between tetramethylammonium groups on adjacent POSS cages during mixing under shear.<sup>43</sup>

Octamethacryl POSS was incorporated in polyvinyl chloride (PVC) obtaining homogeneous and transparent materials with up to 15% wt. POSS, showing plasticisation effect similarly to the classical dioctyl phthalate (DOP) plasticiser. However, using methacryl POSS to plasticise PVC to room temperature-flexible compounds was not possible due to the miscibility limit at about 15% wt.<sup>44</sup> Addition of a small amount of DOP increases the miscibility of methacryl POSS in PVC substantially, leading to  $T_g$  of the ternary PVC–POSS–DOP near room temperature.<sup>45</sup>

**Polyamides.** Melt blending in polyamide 6 (PA6) of two different POSS structures, namely octaisobutyl POSS and trisilanol phenyl POSS, was recently reported.<sup>46</sup> Dispersion of POSS was found to be in agreement with their predicted solubility, estimated on the group molar-attraction contributions. Trisilanol phenyl POSS exhibits greater compatibility, *i.e.* smaller POSS domains (10–50 nm) in comparison to octaisobutyl POSS (>100 nm), as expected from the calculated solubility parameter being close to that of PA6. However, both POSS molecules show preferential segregation to the surface, driven by their low surface energy, and formation of larger aggregates at the surface than in the bulk. Segregation of POSS on the surface strongly affect the material surface properties, including a significant friction reduction (up to 43% reduction with 10% wt. trisilanol phenyl POSS) and improved hydrophobicity.

The use of trisilanol phenyl POSS in PA6 was also proposed to enhance char quality obtained during combustion of polyamide.<sup>47</sup> The effects of trisilanol phenyl POSS in polyamide 12 (PA12) was also addressed, showing that the addition of POSS plays little role in the crystalline transition behaviour of PA12 but enhances the tensile properties (nearly doubles modulus with 5% wt. POSS and unmodified elongation at break) compared with the neat polymer.<sup>48</sup>

Melt blending of PA6 with octaisobutyl POSS or isobutyl POSS, modified with a single PA6 oligomeric chain ( $M_v = 24\,000\text{ g mol}^{-1}$ ), was also reported.<sup>37</sup> While octaisobutyl POSS showed clear phase separation on the microscale, fully homogeneous blend is obtained when the PA6 oligomeric chain is bound to POSS, acting as a compatibiliser toward the Si–O framework and the PA6 polymer matrix.

**Polyesters.** Polyethylene terephthalate (PET) nanocomposites were prepared by melt blending with isoctyl POSS or isoctyl trisilanol POSS and successfully spun into fibres,<sup>49</sup> whereas methyl-, isobutyl- and phenyl- $T_8$  POSS were reported to be incompatible with PET by the same authors. Both fibres containing isoctyl POSS or isoctyl trisilanol POSS showed improved mechanical properties, in terms of higher tensile modulus and tensile strength (by up to about 30%) as well as almost twofold compressive strength. Moreover, dynamic mechanical tests evidenced an increased retention modulus for PET–POSS nanocomposites as compared with neat PET, this reinforcement being much higher for temperatures above the glass transition temperature, especially for trisilanol POSS.<sup>49</sup> Nucleation effect of trisilanol isobutyl POSS in PET was also reported.<sup>50</sup>

Even if no evidences of chemical reactions between silanol groups and PET are brought, strong chemical interactions with the polymer are likely to occur, as discussed in detail in the reactive blending section of this paper.

Vannier *et al.* recently reported the blending of octamethyl POSS in PET, showing extensive aggregation of POSS already at concentrations as low as 1% wt.<sup>51</sup>

**Polycarbonate.** Zhao *et al.* used melt blending to prepare various POSS–polycarbonate (PC) systems, which showed differences in compatibility depending on the filler specific structure, either completely condensed or carrying residual silanol groups.<sup>52</sup> Octaphenyl POSS–PC composites show reduced optical transparency, suggesting limited compatibility, and lower

glass transition temperature. On the other hand, trisilanol POSS molecules provided better compatibility with PC than octaphenyl POSS, explained by the possibility of polar or covalent interactions between POSS and PC (see the reactive blending section of this paper). However, other authors claim that no reactions between trisilanol phenyl POSS and PC occur during melt blending, but these occur only at higher temperature (*e.g.* 380 °C) during the thermal scission of PC, when POSS moieties have an important role in the thermal degradation and combustion processes.<sup>53,54</sup>

Melt blending of unreactive octaphenethyl POSS in PC was recently reported by Sanchez-Soto *et al.*:<sup>55</sup> a submicronic dispersion was achieved up to 5% wt. of nanofiller, whereas micron-sized aggregates were observed at higher loadings. Increasing the amount of nanocages caused a continuous decrease on the PC–POSS glass transition temperature, assigned to a POSS plasticising effect, whereas mechanical properties showed dependency on the POSS amount. Yield stress ( $\sigma_y$ ) and Young's modulus (E) were slightly improved for POSS concentration  $\leq 5\%$  wt., while higher amounts of POSS led to a decrease on both  $\sigma_y$  and E, to values equal or lower than for the neat matrix. On the other hand, a continuous decrease on the strain at break was also observed, reflecting the brittle character of the formed composites. This behaviour was attributed to the presence of micron-sized POSS crystals, proportional to the POSS loading, that cause a restriction to chain mobility overcoming the plasticising contribution.

**General considerations on melt blending of POSS.** From the above reviewed results, obtaining molecular dispersion of POSS into thermoplastic polymers by simple melt blending is not an obvious achievement and often actually results to be very challenging.

This also comes from the fact that POSS has been most often considered and treated as a nanofiller, in analogy with well-known nanofillers such as silica, metal oxides, layered silicates and hydroxides. However, this is not correct in principle, because POSS are organic–inorganic hybrid molecules characterised by defined structures, whereas nanoparticles are, by definition, nano-objects chemically defined by an average composition and size distribution in the 10 to 100 nm scale range. For this reason it is certainly more appropriate to refer to POSS as chemicals, with intrinsic properties which are very different from those of organofunctionalised nanofillers. Thus, the use of the term nanocomposite to identify polymer–POSS mixtures is not fully satisfactory and actually has a proper meaning only when POSS aggregates to build supramolecular structures (*e.g.* layered aggregates<sup>56</sup>) behaving as nanoparticles. However, the opportunity of using POSS to obtain aggregates in polymers is questionable and should be limited to the cases in which bottom-up approach is convenient, *i.e.* when the type of supramolecular structure aimed is difficult or impossible to be obtained by the use of preformed nanoparticles.

In this frame, processing conditions should be tailored taking into account the peculiarity of POSS. In particular, a major role seems to be played by the balance between interactions (van der Waals forces, hydrogen bonding, *etc.*) between POSS and the polymer and POSS–POSS self interactions, rather than shear imposed and total mixing energy imposed. However, a critical

discussion of the role of the mixing conditions (temperature, time, shear forces, *etc.*) cannot be given at this time on the base of reported results, due to the lack of systematic studies on POSS dispersion *vs.* processing conditions as well as to the large variability of POSS structures used in the different polymers.

Given the difficulties in obtaining molecular dispersion of POSS by simple melt blending, the possibility of using a chemical reaction during melt mixing to drive dispersion into the polymer represents an outstanding opportunity, also thanks to the great POSS synthesis versatility. This approach, leading to real organic–inorganic hybrid polymers, is reviewed in the following section of this paper.

### Melt reactive blending

While melt blending leads to physical interactions between polymer and POSS, the preparation of organic–inorganic hybrids in which POSS is covalently bound to the polymer backbone requires a chemical reaction to occur. Despite the fact that *in situ* copolymerisation of POSS to produce organic polymers with pendent silsesquioxane groups has been widely studied, very little work has been reported on the preparation of polymer–POSS hybrids by reactive blending procedures. Indeed, the possibility to perform a chemical reaction between POSS and a polymer to prepare POSS hybrids through a one-step melt blending process represents a very appealing, economic and environmental friendly approach to modify polymer properties and/or to obtain new functionalities.

However, it is worth noticing that reactive blending of POSS is still in its infancy: thus, a comprehensive set of systematic research works still lacks and contradictory results are sometimes found. In this section, results for polymer–POSS hybrids obtained by reactive melt blending are reviewed, distinguishing two different groups of reactions, namely radical grafting and non radical reactions.

**Radical grafting reaction.** The modification of polymer structure by grafting chemical species on its backbone is a well known approach and represents a very interesting method to give new or improved properties to the resulting materials. This approach, widely used for the compatibilisation of immiscible polymer blends<sup>57,58</sup> or for the preparation of functional polymers,<sup>59,60</sup> has been based on different techniques, including thermal, irradiation, photochemical and plasma treatments.

Most research work has been focused on polyolefins, in which free radical grafting processes have been widely studied in order to obtain functionalisation with various organic groups including maleic anhydride, acrylic, methacrylic and vinyl species.<sup>1,61–63</sup> Moreover, different methods have been developed to control the radical mechanism and reduce side reactions, including the use of coagents,<sup>64,65</sup> advanced radical promoters<sup>66</sup> and atom transfer radical polymerisation.<sup>67</sup>

Taking into account the above described literature works, a similar approach has been exploited for the preparation of PP–POSS hybrids.

Zhou *et al.*<sup>68</sup> reported on the exploitation of reactive blending for the preparation of PP–octavinyl POSS compounds by a free radical reaction. It was shown that POSS had better compatibility with PP when blended in the presence of a free radical

initiator, due to partial POSS grafting onto PP chains. Both mechanical properties and crystallisation behaviour were strongly affected by bound POSS, which led to a higher modulus and to a significant increase in nucleation rate.<sup>69</sup> As far as the rheological properties are concerned, the viscosity of the reactive blending composites was found to increase with increasing POSS content.<sup>70</sup> In the case of physical blending composites, the viscosity turned out to drop at low silsesquioxane concentration (0.5–1% wt.) and thereafter it increased with increasing POSS content. Moreover, for reactive blending composites, a solid-like rheological behavior, when POSS content was higher than 1% wt., was found, while physical blending composites exhibited a liquid-like rheological behaviour. Zhou *et al.*<sup>71</sup> compared also thermal properties of the above PP–POSS systems, prepared by both physical and reactive blending, demonstrating that the latter hybrids had better thermal stability than the physical blending ones.

POSS grafting on PP was also explored by *in situ*  $\gamma$ -ray radiation on previously prepared PP–monofunctional methacryl POSS blends.<sup>72,73</sup> Radiation-induced grafting of POSS was confirmed by FT-IR: in particular, the absence of the absorption band at 1640 cm<sup>-1</sup>, which corresponds to the methacrylate double bond, proved that these had all reacted. Moreover, the nanocomposite prepared showed an increase of mechanical properties with increasing POSS content and with the increase in absorption dose up to 5 kGy.

Free radical reactions exhibit however significant limitations; in particular, the process conditions should be carefully studied in order to control the undesired side reactions, including PP degradation by  $\beta$ -scission<sup>60</sup> and POSS homopolymerisation. Although the evaluation of side reactions is a crucial aspect in the development of POSS radical grafting, considering the above described works, this issue has not been taken in proper consideration so far.

**Other reaction mechanisms.** Attempts to prepare poly(ethylene terephthalate) (PET), using differently functionalised POSS, by reactive blending were the first reported. Triepoxy-trifunctionalised cyclopentyl POSS showed phase separation when melt blended with PET, evidencing limited extent of the reaction with the polymer.<sup>74</sup> Similar results were obtained also holding the systems at the mixing temperature for additional time in order to promote the reaction between the PET hydroxyl end groups and triepoxy POSS. On the other hand, both isooctyl POSS and trisilanol isooctyl POSS showed no phase separation and led to increased modulus at high temperature, especially for the trisilanol POSS, which is potentially reactive with PET chain ends.<sup>49</sup> Also Ciolacu *et al.*<sup>75</sup> evidenced the reactivity of trisilanolisobutyl-POSS and PET, the hybrids showing increased thermooxidative stability and lower discoloration.

In the field of polyesters, octaepoxycyclohexyl polyhedral oligomeric silsesquioxane was used to prepare a chain-extended POSS in a twin-screw extruder.<sup>76</sup> Although it was reported that the mechanical and thermal properties of poly(butylene terephthalate) (PBT) were improved when epoxy POSS was added, neither an assessment of the reaction mechanism between the two system components nor an evaluation of POSS dispersion was carried out.

Difficulties of preparing POSS-based hybrids by using the reactive blending approach was assessed also in the case of

polyamide 6 (PA6)–POSS compounds. Indeed, Alongi *et al.*<sup>77</sup> verified that phase separation occurred in the systems prepared by melt mixing in a microcompounder PA6 and both mono-functional or multifunctional epoxy POSS, potentially capable to react with the polymer functionalities. More recently, a similar approach was proposed by Yu *et al.*,<sup>78</sup> who studied the thermal stability of polyamide 1010–POSS composites prepared by melt blending, using both the octavinyl and octaepoxycyclohexyl POSS. This study demonstrated a slower thermal decomposition kinetic of PA–POSS compared to the polymer; however, a detailed evaluation of the features of the composites prepared was not given.

The above illustrated works suggest that the obtainment of POSS-based hybrids, having POSS nanometric distribution, is not straightforward to obtain by the reactive blending approach either. Indeed, crucial aspects should be considered, such as reaction time and temperature, concentration and mobility of reactive groups and that the success of this approach depends not only on the conditions applied but also on the specific polymer–POSS pair. Nevertheless, the following examples demonstrate the effectiveness of the technique, which is capable of promoting POSS dispersion and allows one to obtain novel hybrids, once proper conditions and chemical structures are selected.

Interactions/reactions between silsesquioxane molecules and the polymer have been deeply studied in selected cases. The influence of the specific kind of interactions of POSS with the polymer matrix on the material final properties was studied in the cases of polycarbonate (PC) or phenoxy resin (PKFE)-based composites.<sup>79</sup> While phenyltrisilanol POSS was found to physically interact with PKFE, it turned out to react with polycarbonate. As a consequence of the above different behaviour, the glass transition temperatures of phenoxy composites increased by about 6 °C with incorporation of 10% wt. POSS, while  $T_g$  of polycarbonate composites is reduced as much as 15 °C for the composites containing 20% wt. POSS.

Fina *et al.*<sup>80</sup> reported successful grafting of monofunctional amino POSS (5% wt.) onto maleic anhydride-grafted PP (PPgMA), taking advantage of the amine–anhydride reaction in a one-step reactive blending process. Indeed, the reactivity of PPgMA with model amine (hexamethylene diamine) in the molten state was recently assessed, showing quantitative conversion.<sup>81</sup> Morphological analyses on the obtained materials evidenced POSS dispersion at the nanoscale, whereas the corresponding blend obtained with non-reactive POSS contained residual micron-sized aggregates when processed in the same conditions. As far as the properties of POSS-grafted PPgMA are concerned, the presence of POSS moieties grafted on PPgMA was found to improve the thermo-oxidative stability, in terms of delayed mass loss during thermal degradation under air, as compared to both neat PPgMA and PPgMA containing the correspondent non-reactive POSS. The higher stability towards thermoxidative degradation was explained by the accumulation of POSS on the sample surface during the early stage of PPgMA–amino POSS degradation, thus reducing the radical initiation action of oxygen in the thermal degradation of the polymer. Moreover, POSS grafting on PPgMA chains was shown to radically affect the molecular mobility, resulting in a higher melt viscosity and in a significant stiffness and strength increase.

More recently, Zhou *et al.*<sup>82</sup> demonstrated that maleic anhydride-grafted PP strongly influenced the morphology, crystallization and rheological behavior of the system made of isotactic PP and octaaminophenyl POSS, compatibilised by using PPgMA. Indeed, SEM showed that the PPgMA improved the compatibility between PP and octaaminophenyl POSS and promoted a fine dispersion of the above silsesquioxane in PP matrix, due to the reaction of the amine groups of octaaminophenyl POSS with maleic anhydride groups of PPgMA.

Although the above studies have confirmed the feasibility of reactive blending for obtaining hybrid systems based on PP, the low content of grafted maleic anhydride in commercial PPgMA limited the amount of graftable POSS. On these grounds, Monticelli *et al.*<sup>83</sup> addressed the use of maleic anhydride copolymers and developed novel poly(styrene-*co*-maleic anhydride) (PSMA)–POSS hybrids, with POSS loadings up to 50% wt. As for the PPgMA-based hybrids, the reaction mechanism assessed by means of FTIR measurements, involved the imidization reaction between the MA group of PSMA and the amino group of POSS molecules, with the formation of a cyclic imide linkage binding POSS to the polymer backbone. The grafting kinetics turned out to be controlled by a surface reaction at the POSS crystal–polymer boundary, the selected POSS being a solid in the used blending conditions. This led to the progressive evolution of the microstructure during processing in the mixer, passing from heterogeneous polymer–POSS mixture to biphasic polymer blends, where the two phases contain different concentrations of POSS, and finally to a fully homogeneous PSMA–POSS hybrid phase, corresponding to a complete grafting yield. The phase separation was found to control the thermal and thermomechanical properties of the material. In particular, multiple glass transition temperatures and dynamo-mechanical relaxations ( $T_a$ ) were found, related to the presence of unbound POSS acting as a plasticiser, thus increasing molecular mobility of polymer chains. Films prepared from the PSMA–POSS system containing low amounts of silsesquioxane (up to 10% wt.) turned out to be completely transparent, while the transparency of those based on higher POSS content was achieved only after removing the unbound POSS. Indeed, the hybrids generally showed increased hydrophobicity, regardless of the amount of POSS in the explored concentration range.

The reactive blending approach has also been applied in the field of multi-component systems, studying the effect of the POSS reaction with one or more components of the blend. Indeed, Li *et al.*<sup>84</sup> considered the incompatible blend poly(2,6-dimethyl-1,4-phenylene oxide)/polyamide 6 (PPO/PA6), where PPO had much higher melt viscosity than PA6. In order to increase the viscosity of PA6 to meet that of PPO, octaepoxycyclohexyl POSS was introduced into the above blend by melt blending. In this case POSS was reported to act as a chain extender and a crosslinking agent for PA6, in contrast with previous reports on similar systems,<sup>77,78</sup> affecting the morphology of the composites. Increasing POSS content from 2 to 4 phr, the morphology of the composites transformed from droplet/matrix to cocontinuous morphology and showed improved mechanical properties, in terms of tensile strength (*ca.* +5%), impact strength (*ca.* +50%) and higher elongation at break (about ten times the elongation of reference blend).



The effect of POSS incorporation, namely octavinyl and epoxycyclohexyl POSS, was studied also in the case of a poly(lactic acid)–poly(butylenes succinate-*co*-adipate) blend prepared by melt mixing.<sup>85</sup> While octavinyl POSS existed in the PLA–PBSA blend as crystalline aggregates, octaepoxy-functionalised POSS turned out to be dispersed more uniformly, showing also higher melt viscosity and broader processing window, attributed to the reactions between the epoxy groups of the above silsesquioxane and carboxyl groups of PLA–PBSA. Moreover, particularly in the case of the introduction of epoxy POSS in the blend, the thermal stability of the materials was found to increase mainly because of the reduced hydroxyl and carboxyl end groups and the limited molecular chain mobility which resulted from the reactions.

## Conclusions

Melt blending of POSS into thermoplastic polymers is a promising route to obtain modification of thermal, mechanical and functional properties of polymers, thanks to the versatility of POSS synthesis, which opens the way to insertion of a virtually unlimited variety of functions on POSS structure.

The key point to exploit POSS properties is obviously the capability to disperse these chemicals at the molecular scale. However, despite the intrinsic organic functionalisation brought on POSS, dispersion into polymers by simple melt mixing is not obvious and requires the strict control of the balance between polymer–POSS interactions and POSS–POSS self-interactions. From a general point of view, organic groups chemically similar to the polymer and long enough to provide effective interactions are needed. The solubility limit of POSS depends also on the free volume available to host POSS, namely related to the amorphous fraction in semicrystalline polymers. The role of mixing conditions (temperature, time, shear forces, mixing energy *etc.*) is not yet studied in details, but it is expected that these aspects play a minor role compared to the thermodynamics of mixing.

Chemical reactions between POSS and polymer chains can be taken into advantage to achieve molecular dispersion of POSS and to obtain hybrid organic–inorganic polymers. This approach is certainly very appealing, being a fast, inexpensive and environmental friendly method to obtain new materials with controlled structure and properties. However, the study of reactive blending methods with POSS is still in its infancy and requires much effort to reach the challenging goal of obtaining hybrid materials bridging the gap between organic polymers and ceramics.

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