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NANOFIRE

Environmentally friendly multifunctional fire retardant polymer hybrids and nanocomposites

STRP RTD Project

PRIORITY [3] “NANO-TECHNOLOGIES AND NANO-SCIENCES, KNOWLEDGE-BASED MULTIFUNCTIONAL MATERIALS AND NEW PRODUCTION PROCESSES AND DEVICES”

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Report on the actual state of the art of nanocomposite materials

Polymer nanocomposites by melt blending

In polymer nanocomposites (PN), a few wt.% of each filler is randomly and homogeneously dispersed on a molecular level in the polymer matrix. When molded, the mechanical, thermal and barrier properties of these materials are superior to those of pristine polymers and/or conventional composites. The effects are very striking, and have become well known since many excellent reviews have been published [1-3]. Polymer clay nanocomposites were first reported in 1985 by Toyota Central R&D Labs, Inc. (Toyota)[4]. They bore a new concept of polymer nanocomposites, expanded the field of polymer science including preparation, structure and interfaces and led to new applications for automotive, electric and food industries.

The major use of polymers is in molded products. Polymers have been successfully reinforced using glass fiber, talc, calcium carbonate, carbon black and other inorganic fillers. The content of the filler is usually between 20 and 40 wt.% of a composite, and sometimes exceeds 50 wt.% in thermosetting resins. Polymers and fillers are not homogeneously mixed on a microscopic level, and are composed of different phases. The interface is not large, and interaction between the polymer (matrix) and the filler is limited. Takayanagi et al. proposed the concept of a molecular composite, on the basis that if the filler is of molecular size then mechanical properties could be further improved, and showed an example of a nylon matrix containing aramide fiber whose content was 5 wt.% and diameter was 30 nm [5]. If fillers of nm dimensions were used instead of fibbers, the contact surface would become much larger.

Polymer layered silicate nancomposites

Smectite clay minerals, especially montmorillonite (MMT), are potential candidates for a platelet-type filler for molecular composites, since they are composed of several layers of silicates.

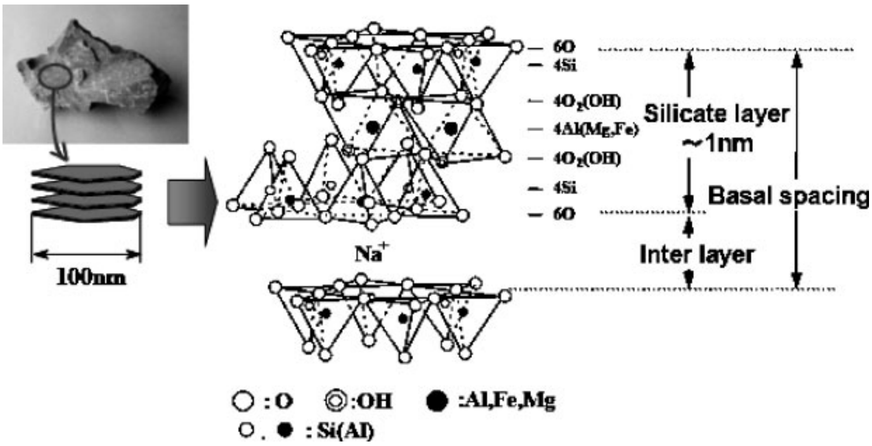

Figure 1: Structure of montmorillonite

These silicates are 1 nm thick and have a cross-sectional area of 100 nm^2, which is very small compared to conventional fillers and also aramide fibers. MMT is the most common and ubiquitous clay mineral, and it is well known that it undergoes intercalation and swelling in the presence of water and organic cations [6].

Syntheses of polymers in the presence of MMT have previously been reported [7] but their major component was clay, and these studies were not intended to improve polymers but rather to focus scientific interest.

Polymer clay nanocomposites are classified into the "intercalated" type, where the structure of the clay is maintained to some extent, and the "exfoliated" type, where silicate is randomly and homogeneously dispersed. If the silicates are in such a state, interactions between them must be avoided and the interface area is enormous. Actually, it was discovered that when the clay content was less than 5 wt.%, such a molecular composite, hybrid or nanocomposite could be obtained. The structure of MMT is shown in Fig. 1, and scanning electron microscopy (SEM) photographs of glass fiber and clay in the polymer matrix are shown in Fig. 2, where the scales of two photos differ by 100 times.

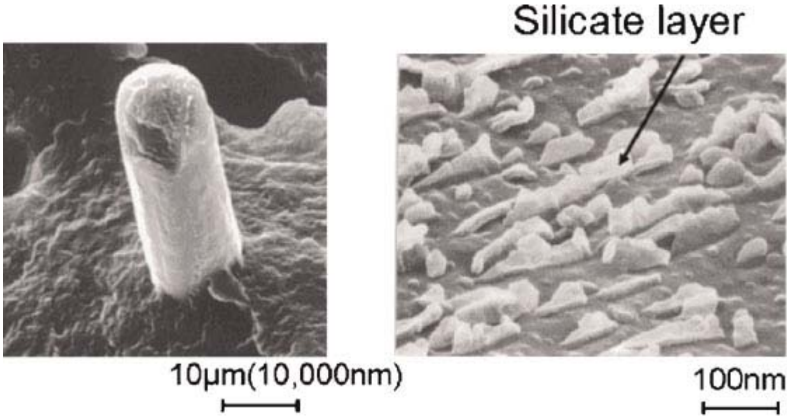

Figure 2: Comparison of size of glass fiber and montmorillonite in PA6 based nanocomposites

Although the high aspect ratio of MMT is ideal for reinforcement, the nanolayers are not easily dispersed in most polymers due to their preferred face-to-face stacking in agglomerated tactoids. Dispersion of the tactoids into discrete monolayers is further hindered by the intrinsic incompatibility of hydrophilic layered silicates and hydrophobic engineering plastics. However, as was first demonstrated by the Toyota group more than 10 years ago [8], the replacement of the inorganic exchange cations in the galleries of the native clay by alkylammonium surfactants can compatibilize the surface chemistry of the clay and the hydrophobic polymer matrix. ε-Caprolactam was polymerized in the interlayer gallery region of the organoclay to form a true nylon 6–clay nanocomposite [9]. At a loading of only 4.2 wt.% clay, the modulus doubled, the strength increased more than 50%, and the heat distortion temperature increased by 80°C compared to the pristine polymer (see Table 1).

Table 1: Mechanical and thermal properties of nylon 6–clay composites

Composite type	**Clay (wt.%)**	**Tensile strength (MPa)**	**Tensile modulus (GPa)**	**Impact (kJ/m^2)**	**HDT (°C) @ 18.5 kg/cm$_2$**
"Nanoscopic" exfoliated	4.2	107	2.1	2.8	145
"Micro" tactoids	5.0	61	1.0	2.2	89
Pristine Polymer	0	69	1.1	2.3	65

They also demonstrated that organoclays exfoliated in a nylon 6 polymer matrix greatly improved the dimensional stability, the barrier properties and even the flame retardant properties [10-11].

Several strategies have been considered to prepare polymer-layered silicate nanocomposites. They include three main processes:

- Intercalation from a polymer solution: the layered silicate is exfoliated into single layers using a solvent in which the polymer is soluble. It is well known that such layered silicates, owing to the weak forces that stack the layers together can be easily dispersed in an adequate solvent. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated (or the mixture precipitated), the sheets reassemble, sandwiching the polymer to form, in the best case, an ordered multilayer structure.
- In situ polymerization: in this technique, the layered silicate is swollen within the liquid monomer (or a monomer solution) so as the polymer formation can occur in between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator or by an organic initiator or catalyst fixed through cationic exchange inside the interlayer before the swelling step by the monomer.
- Melt intercalation: the layered silicate is mixed with the polymer matrix in the molten state. Under these conditions and if the layer surfaces are sufficiently compatible with the chosen polymer, the polymer can crawl into the interlayer space and form either an intercalated or an exfoliated nanocomposite. In this technique, no solvent is required.

Focusing our attention on the third preparation method: nanocomposites can be processed using currently available techniques such as extrusion for thermoplastic polymers, thus lowering the barrier towards commercialization.

Thermodynamics that drives the intercalation of a polymer inside a modified layered silicate while the polymer is in the molten state has been approached through a lattice-based mean field theory by Vaia and Giannelis [12]. They found that, in general, the outcome of polymer intercalation is determined by an interplay of entropic and enthalpic factors. In fact, although the confinement of the polymer chains inside the silicate galleries results in a decrease in the overall entropy of the macromolecular chains, this entropic penalty may be compensated by the increase in conformational freedom of the tethered alkyl surfactant chains as the inorganic layers separate, due to the less confined environment.

Liu et al. [13] have prepared nanocomposites based on a commercial nylon-6 melt blended with an octadecylammonium-exchanged montmorillonite (CEC.100 meq/100 g) in a twin screw extruder. They prepared composites with a filler content ranging from 1 to 18 wt.%. An intercalated structure was observed to be formed by XRD for composites containing more than 10 wt.% of the organoclay, with an interlayer spacing increasing from 15.5 Å for the pristine organoclay to 36.8 Å for the intercalated species. At filler content lower than 10 wt.%, no interlayer spacing could be detected through XRD and the TEM micrographs allow for the observation of an exfoliated structure, indicating that exfoliation in this case is highly dependent upon the filler content. XRD and DSC data also showed that exfoliated structures strongly influenced the nature of the nylon-6 crystallization, favoring the formation of ▯-crystals in addition to the crystals of the ▯-form observed in the native nylon-6 matrix. Moreover, DSC cooling scans showed that exfoliated layered silicates highly increased the crystallization rate, having a strong heterophase nucleation effect.

The dispersal of clay nanolayers into the nonpolar polyolefin systems proves to be a challenge since the polarity of organoclay does not match well with such polymers. Poly(propylene) is the most widely used polymer in the automotive industry and in commodity products. While it is less expensive, its mechanical and thermal properties are inferior to engineering plastics such as nylons. However, there is a strong need to improve the mechanical properties of poly(propylene), owing to its low price. After nylon 6 was successfully developed, various research efforts were made worldwide to reinforce PP using clay, but to the best of our knowledge no successful examples of reinforced PP based nanocomposites have yet been reported. No direct intercalation of polypropylene in simply organically modified layered silicates has been observed so far. Since clay is hydrophilic and PP is hydrophobic, there is enormous difficulty in making nanocomposites. Initial attempts to create polypropylene–clay hybrids were based on the introduction a modified polypropylene with polar groups to mediate the polarity between the clay surface and bulk polypropylene [14-15]. However, an organic solvent has to be used in order to facilitate the formation of a modified polypropylene intercalate. Only a limited degree of clay nanolayer dispersion was observed by this method. An alternative and more environmentally friendly approach was developed later by the Toyota research group [16-18]. The mixture of stearylammonium-exchanged montmorillonite, maleic anhydride modified polypropylene oligomer (PP-MA)) and homopolypropylene was melt processed to obtain a successful polypropylene–clay hybrid wherein a larger fraction of the clay nanolayers were found to be exfoliated. They prepared MMT organized with octadecylammonium salt (C18-MMT), and compounded PP-MA using an extruder, successfully giving MMT intercalated-PP-MA. This was then compounded with pristine PP, also using an extruder. All final products contained 5 wt.% of clay. The hydrolyzed maleic anhydride polypropylene intercalated into the organoclay, expanding the galleries, and facilitated the incorporation of polypropylene. Compounding of C18-MMT, PP-MA and PP at the same time also proved to give an exfoliated product. Interestingly, the density of maleic anhydride groups has a significant effect on the final morphology and properties of the composite. The TEM and microscope studies indicated that while the MA unit is necessary for exfoliation, its presence in excess amounts seems to decrease compatibility with the pristine PP. A mixture of roughly 3:1 by mass of maleic anhydride polypropylene oligomer to organoclay was found to be the most effective in forming hybrid composites. The hybrids exhibit improved storage moduli compared to pristine polypropylene in the temperature range from T_g to 90°C. The significance of nanolayer reinforcement in polypropylene is not as great as in nylon 6, probably due to the lower degree of exfoliation and the introduction of a large amount of oligomer. However, polypropylene–clay nanocomposites are still attractive for applications as packaging materials where enhanced barrier properties are desired.

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Polymer nanocomposites based on carbon nanotubes

Carbon nanotubes (CNTs) are currently one of the fundamental research topics in the field of material science. The scientific and industrial interests involve both their synthesis [1] and their application in many research areas [2-3]. CNTs were discovered by Iijima [4] as elongated fullerenes in 1991.

A single-wall carbon nanotube (SWNT) is best described as a rolled-up tubular shell of graphene sheet (Fig. 3) which is made of benzene type hexagonal rings of carbon atoms. The body of the tubular shell is thus mainly made of hexagonal rings of carbon atoms (in a sheet), whereas the ends are capped by half-dome shaped half-fullerene molecules. The natural curvature in the sidewalls is due to the rolling of the sheet into the tubular structure, whereas the curvature in the end caps is due to the presence of topological defects (pentagonal rings) in the otherwise hexagonal structure of the underlying lattice. The role of a pentagonal ring defect is to give a positive (convex) curvature to the surface, which helps in closing the tube at the two ends.

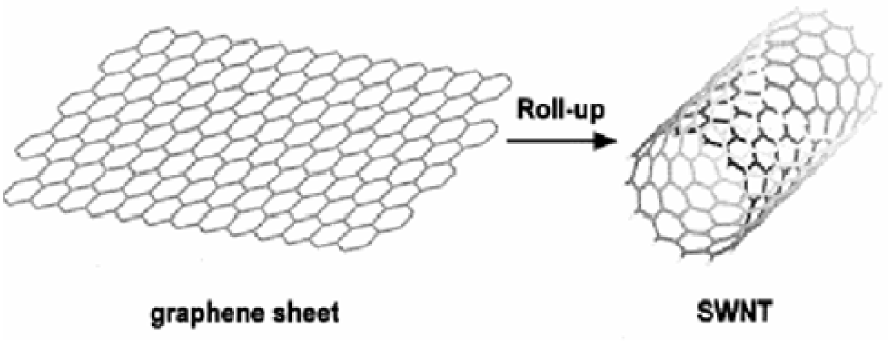

Figure 3: Scheme of SWNT origin from a grapheme sheet

A multi-wall carbon nanotube (MWNT) is a rolled-up stack of graphene sheets into concentric SWNTs, with the ends again either capped by half-fullerenes or kept open.

Soon after the discovery of CNTs, it was realized that the theoretically predicted properties of these very interesting structures, including high strength, high stiffness, low density and structural perfection, could make them ideal for many technological applications. CNTs can be synthesized by several different methods. The most common technique for their production uses an arc discharge through graphite electrodes under a continuum inert gas flow [5-6]. In this process amorphous carbon and possibly fullerenes are also produced; the synthesized CNTs have lengths that do not exceed some micrometers. For the formation of purer CNTs, a more expensive graphite pyrolysis laser technique was used [7-8]. In more recent years, processes of chemical vapour deposition (CVD) of reactive hydrocarbon gases (mostly propane or acetylene) with the use of metal catalysts (Fe, Co, Ni) dispersed on silica [9-11] or alumina [12-14] were proposed, leading to higher yields and wide scale productions. This preparation method can be considered one of the most promising for the large scale use of CNTs in technological applications (i.e. polymer nanocomposites) and there is nowadays an open struggle between producers to reduce prices and improve yield and purity of the products. Finding easy ways to achieve CNTs can however open the way to an industrial scale and cost effective production and make them extremely interesting in the field of material engineering. In fact, the development of polymer nanocomposites based on CNTs and the study of their properties can result in new highly performing materials, because of the extraordinary mechanical, electrical and thermal properties of CNTs. The additivation of small quantities of carbon nanofillers in polymer matrices has shown how the effects of filling are not basically due to the "*bulk*" quantity of the added filler, but mainly to the intimate interfacial interactions between the two phases [15] as in the case of the other nanofillers. For these reasons, CNTs can effectively have an enormous impact on the current polymer materials. However, nanoscaled additives having extremely large surface area and well defined structure and morphology are deemed to be the key to novel composite materials with enhanced physical and chemical properties. While each method has its advantages in terms of physical control and process costs, the importance of understanding how to incorporate these nanofillers into a polymer matrix has been underestimated for a long time. In fact a good control over various parameters is essential to obtain homogeneous composite materials with satisfactory physical, mechanical and chemical properties.

As in the case of polymer silicate layered nancomposites, there are three main routes to produce nanocomposites: the dispersion of CNTs in a polymer solution and then the evaporation of the solvent; the dispersion of CNTs in a monomer and then its polymerization; the melt compounding. Evidently, this method would be preferred in an industrial environment, thus it is being explored with growing frequency.

The use of CNTs as reinforcing nanofillers for polymer materials is still a developing field from both theoretical and experimental perspectives. Computations involving nanocomposites based on CNTs dispersed in a polymer matrix are scarce. An example is the investigation of the molecular mechanics in CNT based nanocomposites by means of a force field molecular model. The binding energies and the frictional forces between CNTs and polymeric matrices were found to play a minor role to determine the interfacial strength. In fact, the key factor is the helical conformation of polymer macromolecules around the nanotube [16]. Also another method for computing the reinforcing effects of CNTs in a polymer nanocomposite was reported [17]: the main premise was the similar size of macromolecules and CNTs, thus the basic assumption of continuum mechanics was not valid. In nanocomposites containing CNTs the polymer/nanotube interactions depend on the local atomic structure and, as a consequence, the bulk mechanical properties of the material cannot be determined through traditional methods based on continuum mechanics. The adopted approach involved the determination of a representative volume element of the molecular structure for the nanotube and the adjacent polymer chains by means of molecular dynamics simulations and then the design of an equivalent continuum model for the representative volume element.

Several works, based on direct HR-TEM or on Raman spectra, indicate slippage between the concentric shells of MWNTs, between SWNTs in a bundle and between CNTs and polymer matrix. Evidently, the slippage takes place at higher strains, hence it affects the tensile strength of nanocomposites, but it does not influence the initial modulus. The basic question is whether polymer/nanotube bonding may solve the problem: the serious danger is the possible significant reduction of the mechanical properties due to the change of CNT structure [18].

An attempt to simulate the effect of covalent bonding between CNTs and either a crystalline or amorphous polyethylene matrix was more recently proposed. This system was used as a model for the initially non-bonded interface and the simulations indicated a remarkable change in shear properties if the polymer matrix was grafted to the CNTs [19]. The bulk mechanical properties for various CNT lengths, volume fractions, orientations and CNT/polymer interfacial characteristics were computed for systems based on polyimide and polyethylene matrices. The results indicated a better adhesion to the polymer for the modified CNTs, but also the drawback of obtaining poorer overall mechanical performances than in case of non-modified ones where only Van der Waals interactions between CNTs and matrix occurred [17,20]. Moreover, for SWNTs dispersed in an amorphous polyethylene matrix the computation of mechanical properties was very significant as it allowed to compare the behaviour of polymer nanocomposites containing long or short CNTs. In both cases mechanical loading in the axial and transverse direction to the SWNTs was applied: the system with long SWNTs was highly anisotropic, with greatly increased modulus in the draw direction, while the system with short SWNTs did not show an increase in modulus compared to the polymer matrix [20].

Since the discovery of CNTs [4] and the realization of their unique properties, many researchers have tried to prepare advanced nanocomposite materials that exhibit one or more of the above described properties [21-22]. If compared to traditional carbon black microparticles CNTs are quite effective as conductive filler in polymers, especially for their high aspect ratios. An increase in electrical conductivity of four orders of magnitude (to 0.01 S/m) was reported for a 0.1 vol.-% CNT loaded epoxy matrix [23]. Moreover, CNT/polypirrole nanocomposites were produced by electrochemical deposition of polypirrole onto CNTs in well aligned arrays. The coating process was controlled by the film formation charge and uniform thickness was obtained, changing the morphology from coated individual CNTs to a uniform conductive material by the filling of the gap between all CNTs in an array [24]. CNTs possess one of the highest known thermal conductivity [25], which suggests their use in composites for thermal applications. Crude SWNTs with a broad distribution of diameters and lengths were employed to produce CNT/epoxy nanocomposites and in particular to increase the matrix thermal conductivity. A 1 wt.-% CNT loading caused a 70% increase in thermal conductivity of the material at 40K, rising to 125% at room temperature [26]. One of the main potential applications of CNTs in the field of polymer nanocomposites is their use as discontinuous reinforcement. CNTs can be considered as the ultimate carbon fibers with yield strengths reported as high as 200 GPa and an elastic modulus in the 1TPa range [27]. These properties, coupled with a surface area approximately 500 times higher than carbon fibers and aspect ratios of around 1000, has aroused a great interest in employing CNTs as a reinforcing phase for polymer matrices. However, after about fifteen years of research, their potential as reinforcement for polymers has not been fully realized even though the mechanical properties of nanocomposites have fallen short out of predicted values. In any case a better understanding of the relationships between processing, interfacial optimization and composites properties is a major goal of this area of research, which may lead to optimal reinforcement of polymer matrices with CNTs [28].

An increasing attention is being focused on the CNT surface, namely the interface between the CNT and the surrounding polymer matrix. Numerous researchers have attributed lower than predicted nanocomposite properties to a lack of interfacial bonding [29]. The surface of a CNT is an exposed graphene sheet and it is not surprising that interfacial traction is a concern. It is the weak interplanar interaction of graphite that provides its solid lubricant quality and resistance to matrix adhesion. This effect is greatly increased by the chemically inert nature of graphene structures. The optimization of CNT/polymer interface for nanoscale mechanical reinforcement is not whole clear yet, but the available evidences indicate that solutions based on chemical means can be effective [28]. Significant improvements in mechanical properties of polymer matrices through the incorporation of CNTs have been reported. A 1 wt.-% of MWNTs, randomly distributed in an ultra-high molecular weight polyethylene film, was reported to increase the tenacity by 150% and the ductility by 140%. Secondary crystallites, which nucleated from the CNTs, were attributed a higher mobility and hence the increase in mechanical properties [30]. A similar effect was found in aligned MWNT/polyacrylonitrile fibers containing 1.8 vol.-% CNTs with an approximately 80% increase in yield and break strength [22]. Slippage between CNT bundles was suggested as the mechanism responsible for the enhancement in the toughness. The addition of 1 wt.-% MWNTs to isotactic polypropylene was shown to affect crystal nucleation from differential scanning calorimetry and X-ray diffraction measurements [31]. If compared with neat polymer, there was an increase in crystallization rate for the nanocomposite material with evidence of fibrillar crystal growth rather than spherulite growth. These morphology modifications combined with the energy required for CNT debonding suggest that CNTs can increase the toughness characteristics of the nanocomposite. A twofold increase in the tensile fatigue strength for an aligned SWNT/epoxy composite in comparison to typical carbon fiber/epoxy composites was found [32]. CNTs can effectively prolong the formation of microcracks that are able to propagate and lead to fatigue failure. CNT reinforced nanocomposites are seen as a potentially fruitful area for the preparation of new tougher or fatigue resistant materials. Further investigations into the toughness and fatigue properties of these composites are needed to better understand the reinforcing mechanism. Tensile strength and modulus enhancements are often reported [28,33], but very few data achieve the predicted reinforcement, especially at loadings beyond 10 vol.-% [34-35]. Some researchers have offered new explanations and factors contributing to understanding this discrepancy between experimental and predicted results. In a two paper series using finite element analysis and micromechanical methods, it was proposed that observed curvature of dispersed CNTs significantly reduced their reinforcement capabilities (by factors from 50 to 200) compared to straight CNTs. It was also noticed that other indistinguishable factors contribute to the discrepancy between the measured and predicted data, including weak interfacial bonding, insufficient dispersion and degradation of the CNTs during the processing [35]. At very low strains, it was suggested that the effect of poor interfacial shear strength should not affect the composite's modulus, implying a measurable elastic response below the strain that causes detrimental effects to the CNT interface. It was also suggested that the diameter distribution of dispersed CNTs would have a very strong effect on the composite's modulus [36]. In the case of MWNTs, an effective modulus was deduced assuming that the outer shell carries essentially all the load [37], such that the modulus was reduced in proportion to the ratio of its sectional annular area to the total sectional area. A MWNT diameter distribution was therefore essential for an accurate prediction of the composite's modulus [36]. It should be feasible to increase the modulus of a polymer/CNT composite beyond the value achievable with high modulus graphite fiber. The alignment of CNTs in polymer matrices is very important for the enhancement of mechanical properties and it has been carried out most often by means of shear or elongational flow [22,30,34] and recently by a magnetic field [38], resulting in film and fiber geometries. However, strengthening of polymer/CNT nanocomposites is less commonly reported. As CNTs have a small number of defects per unit length, their most impressive mechanical property is their tensile strength with recent experimentally measured values up to 150 GPa for MWNTs [39]. These high strengths imply break strains of approximately 10% with even higher break strains reported in the literature. The tensile failure of MWNTs that carry the load within the outer shell is initiated by the formation of a Stone-Wales defect in which 2 C-C bonds are broken and 2 new C-C bonds are formed such that a pair of pentagons and a pair of heptagons results: an increasing number of these dislocations leads to the failure of the CNTs [40,41]. Often, however, in a polymer/CNT composite a reduction in strength is observed and it seems to mean that CNTs can promote crystalline defects in the matrix or, considering their size, act as defects themselves.

There is a high level of interest in using nanometre size particles to produce polymer nanocomposites with very remarkable properties. One of the most promising applications involves the improvement in flammability properties because polymers are combustible under certain conditions. These filled systems are attractive as possible alternatives to conventional flame retardants and furthermore they could simultaneously improve both physical and flammability properties. At present, the most common “nanometre” approach is based on layered silicate nanocomposites, but CNTs are another candidate as a flame retardant additive because of their highly elongated shape and consequently their high aspect ratio. For example this effect was demonstrated by the employment of MWNTs in polypropylene [42-43] and also in poly(ethylene-vinyl acetate) [44]. Nanocomposites based on polypropylene and MWNTs (up to 2 vol.-%), obtained by melt blending, are found to significantly enhance the thermal stability of the polymer and to greatly reduce the heat release rate of the matrix during a combustion process. In particular they are at least a flame retardant as effective as nanocomposites based on layered silicates. During the combustion, CNTs allow the formation of a continuous protective layer which is critical for the significant reduction in heat release rate because the layer acts as a thermal shield against the energy produced by the flame [43]. Also SWNTs have potential as flame retardants by the same mechanism, but despite reports of the exceptional physical properties of nanocomposites based on SWNTs [45-47], the studies on their flammability behaviour are scarce. However a recent work [48] investigated the effects of small quantities of SWNTs and their dispersion degree in polymethylmethacrylate on the flammability properties of the relative nanocomposites. The formation of a protective network layer covering the entire surface of the material without any cracks or openings is critical for reducing the heat release rate and the mass loss rate of nanocomposites during the combustion process. In this work the importance of the protective layer was clearly demonstrated and its characterization was needed to understand how it increases the flammability properties of the matrix. In case of a 1 wt.-% SWNT loading in polymethylmethacrylate, a network structure consisting of bundled CNTs was detected. The residue of the combustion was strong enough to be readily handled without breaking it. However, the studied samples shrank during the process and the thickness of the residue was much less than the thickness of the residue obtained with the same quantity of MWNTs. Possible reasons for this difference could be the aspect ratio of MWNTs (large diameter, long tubes) that was larger than in case of SWNTs (very small, relatively short tubes) or the size distribution of the former that was very large compared to relatively narrow size distribution of the latter. The network structured layer, made of large size distribution and high aspect ratios CNTs, might yield a physically stronger layer than that one made of CNTs having narrow size distribution and small aspect ratios. However, the results indicated that the addition of CNTs slightly increased the amount of the residue of combustion and the samples with poor nanotube dispersion generated less residue than in case of a good CNT dispersion. The thermal characteristics of the network structured layer are important to determine the flame retardant effectiveness of the nanocomposites: a test was conducted to measure the transmission of an external radiant flux and also the thermal insulation performance of the layer. It was demonstrated that the thermal conduction through the network layer appears to be negligible if compared to the radiative transfer. The external radiant flux was absorbed at the top layer of the residue and it heated the layer nearly instantaneously for its low density. The hot top layer re-emitted radiation to the gas phase and also to the inside of the residue as a heat loss. Since the heat-up time of the layer was almost instantaneous for its low density, achievement of steady state radiative transfer through the residue was very quick. The network structured layer acts as a thermal shield to reduce the exposure of the polymer to an external radiant flux.

If nanocomposites have a poor CNT dispersion or a low content of CNTs (0.2 wt.-% or less), they form numerous black discrete islands and vigorous bubbling is observed between the islands during the combustion process. The heat release rate of the nanocomposite which formed the network structured layer is about a half less than those which formed the islands. It was proposed that the formation of the islands depends on localized accumulation of CNTs as a result of bubble bursting at the surface and bubble induced flow from inside the sample to the surface through the molten sample layer. The network structured layer mainly consists of CNTs with a small amount of hydrocarbons and amorphous carbon and it acts as a heat shield to slow the thermal degradation of polymethylmethacrylate [48].

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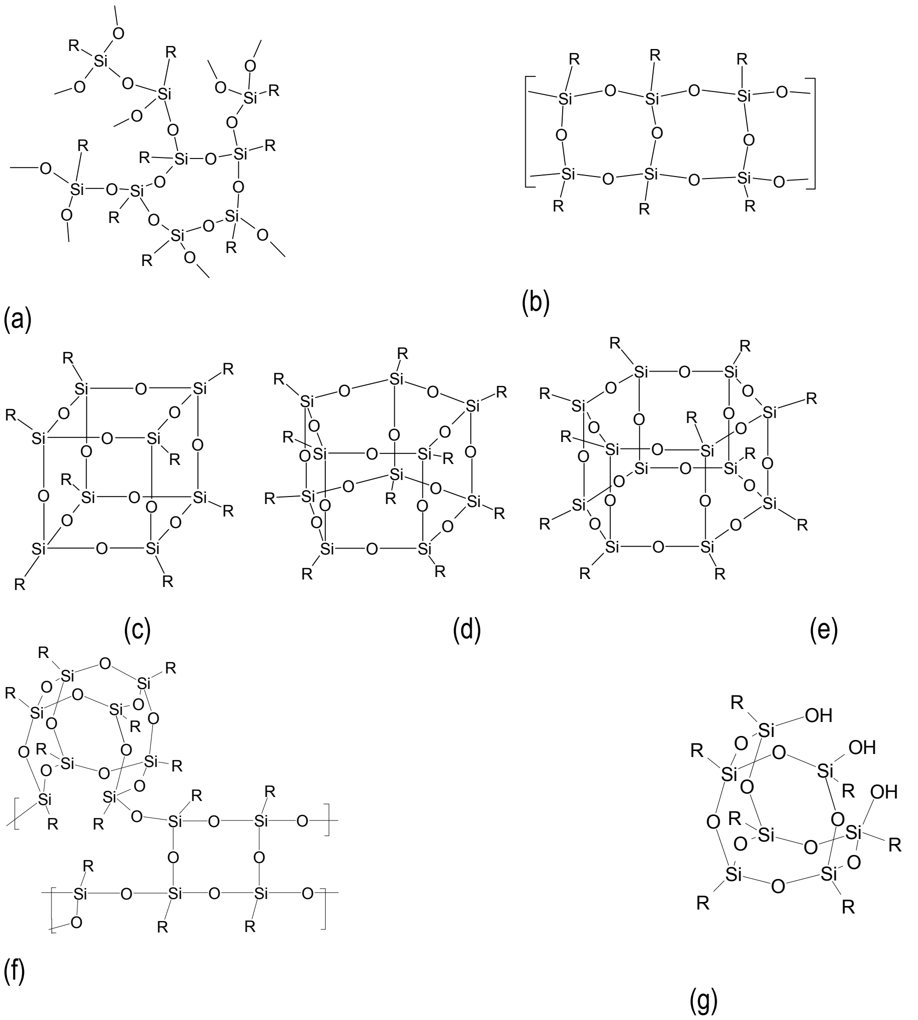
Silsesquioxane-based polymer nanocomposites

Silsesquioxanes are a class of organosilicon compounds with general formula $(RSiO_{1.5})_n$ where n is an even number and R is hydrogen or an organic group, such as alkyl, aryl or any of their derivatives. Each Si atom is therefore bound on average to 1.5 oxygen atoms (giving the prefix sesqui-) and to an hydrocarbon group (giving the –ane termination). Very different silsesquioxane structures have been prepared and studied, with different degrees of symmetry (Fig. 4), including random structure (a), ladder structures (b), polyhedral structures (c, d, e), as well as mixed structure (f) and incompletely condensed polyhedra (g) [1,2].



(a) (b) (c) (d) (e) (f) (g)

Figure 4: Silsesquioxanes geometrical structures: a) random, b) ladder, c) T_8 POSS, d) T_{10} POSS, e) T_{12} POSS, f) mixed cage-network structure and g) incompletely condensed POSS

Polyhedral structures are the most widely studied silsesquioxanes, being also known as POSS from the acronym for Polyhedral Oligomeric SilSesquioxanes (POSS is a trademark from Hybrid Plastics).

It is worth noticing that molecular structure sketches reported in Fig.4 are not representative of the real steric volume of the R groups, that may represent the major POSS volume fraction. As a rough estimation, diameter of POSS molecules is variable from 1 to 3 nm, depending on the size of R groups, whereas diameter of the cubic (T_8) Si-O cage is about 0,5 nm.

POSS are particularly interesting when aiming to tailor the properties of a polymer based materials by the modification of the macromolecular structure; in this sense POSS are the nanoscale building blocks for new materials. POSS are based on an Si-O-Si thermally and chemically robust inorganic core which is the smallest possible silica particle, being also known as molecular silica. At the same time, the possibility to choose the group on POSS surface permits the solubility within the organic matrixes, while the possible presence of reactive groups allows chemical bonding onto the organic macromolecules. On the whole, POSS are highly tailorable and controlled structures: the ideal nanoparticle for a molecular level reinforcement of organic polymers (Fig. 5).

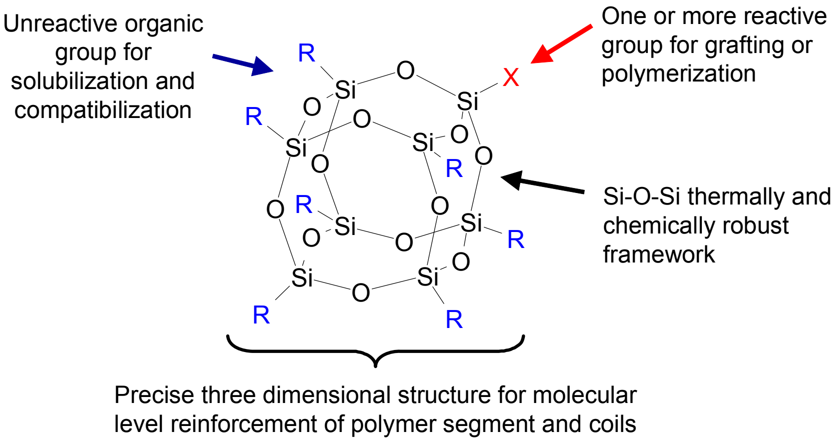


Figure 5: POSS features

Generally, the increase of the R organic chain length corresponds to a lower melting point, a lower density and a higher solubility in organic moieties. With the same organic substituent, higher melting point and lower volatility is observed with T_8 cubic structure, evidencing their higher crystalline stability with respect to larger Si-O cage structures.

Despite the fact that POSS were discovered in the middle of 40s [3] and several studies were carried out in General Electrics [4] and Dow Corning research laboratories as well as in different universities [5-8], it is just in the last decade that POSS have found the applications that determined the development of a worldwide research interest on these materials. The main milestone in POSS technology development is certainly the study, carried out since the early 90s at the US Air Force Research Laboratory in California, on POSS based hybrids for high performance materials to be used in aerospace applications, such as for tanks, piping, high temperature shields, lubricants and coatings [9]. The stated objectives in this pioneering research were the increase of the maximum use temperatures, the reduction of weight and improvement of mechanical properties as well as oxidation resistance and fire behaviour.

On the basis of this background, in the middle of the 90s a private spin-off society named Hybrid Plastics was established to produce and commercialise POSS on large scale. Hybrid Plastics nowadays produces a large catalogue of commercially available POSS, pricing in the range of 1$/g, depending on the organic functionalisation. The high POSS cost is probably the main limiting factors for the development of large scale industrial applications; a large price reduction was in fact expected in the last years, but quotations remained approximatively stable during the last three years.

POSS pricing seems to depend on commercial strategy rather than reflecting synthesis costs; Hybrid Plastics is in fact the only producer, thanks to its World Patents [10,11].

Different synthetic routes have been reported after first preparation by Scott [3], each involving sol-gel processes. Detailed mechanism for the synthesis of silsesquioxanes have been reported [2,12]. The reaction is generally a controlled hydrolysis on a $RSiY_3$ precursor followed by condensation, Y being a highly reactive organic group, usually alkoxy (-OR', with R'=H, methyl or ethyl) or chlorine (-Cl):

$$n\,RSiY_3 + 1.5n\,H_2O \rightarrow (RSiO_{1.5})_n + 3n\,HY$$

Parameters controlling this reaction include: R and Y group chemical nature, solvent, temperature, pH, reaction time, and amount and rate of water addition.

Tailoring these reaction parameters, different POSS structures can be obtained [2,13], as reported in Fig. 4.

There are basically three main synthetic ways to prepare and modify POSS:

- Direct complete condensation: complete condensation of $RSiY_3$ precursors leads to the formation of a polyhedron (Fig. 5). In general, complete condensation is favoured with small R groups, whereas difficulties are found with large and rigid organic groups, due to their steric hindrance. The synthesis of completely condensed POSS have been reported with several R substituents, including methyl [14-16], ethyl [15-17], n-propyl [15], butyl [15], n-pentyl [18], n-hexyl [19], ciclohexyl [15], phenyl [15,20,21], benzyl [22] and with other substituted phenyl groups [19,23]. The POSS thus obtained can be further modified by a second step reaction involving the R groups, depending on their chemical reactivity. Another possibility is to perform hydrolytic condensation from a mixture of different precursors, to obtain different R and R' groups on the POSS cage, depending on molar ratio and chemical reactivity.
- Incomplete condensation-corner capping reaction: incompletely condensed POSS structures can be obtained depending on the synthetic conditions; in particular, a trisilanol "open cage" with one missing corner (Fig. 4g) is easily obtained with high steric hindrance substituents, such as cyclopentyl and cyclohexyl [5,6,24]. This incomplete cage can be corner capped with a functional $R'SiY_3$ to obtain a monofunctional complete POSS cage, allowing a precise control on the final POSS structure. This approach is particularly interesting for the synthesis of metal functionalised POSS [2, 25], which have been used as homogeneous and heterogeneous catalysts for alkene polymerisation, alkene methathesis and alkene epoxidation [26].
- Hydrosilylation: is a way to modify completely condensed POSS, through reaction on a double bond [1,27]; this is possible both on hydro-POSS and on POSS functionalised with unsaturated-end chains. This reaction requires a catalyst, usually a Pt based complex, such as the Karstedt catalyst.

In the past decade, researchers' interest has been widely attracted by the possibility to prepare hybrids and nanocomposites starting from inorganic cage molecules constituted by a silicon-oxygen based framework.

Several polymeric systems have been taken in to account incorporating POSS cages both in thermoplastic matrices, such as styryl-based polymers, acrylates, olefins and in thermosets, mainly as regards epoxy resins [28]. From a general point of view, the presence of the thermally robust POSS moiety was found to drastically modify the polymer thermal properties supplying greater thermal stability to the polymer matrix, also allowing the tailoring of the polymer glass transition temperature by tuning the POSS concentration. Moreover, incorporation of POSS molecules was responsible for improvements of the mechanical properties as well as reductions in flammability and heat evolution in combustion.

The preparation of POSS-polyolefines hybrids by copolymerisation has been widely studied; two main preparation routes have been reported [28]:

- Ring opening metathesis copolymerisation (ROMP): involving the ring opening of a cyclic polyolefin (e.g. cyclooctene) and subsequent reaction with a norbornene-functionalised POSS, in presence of Grubbs catalyst [29-32]
- Metallocene catalysed copolymerisation: of ethene (or propene) with double bond-functionalised POSS [33] or norbornene POSS [34], activated by methylalumoxane (MAO).

On the opposite, Ziegler-Natta polymerisation is not effective in POSS copolymerisation, because of POSS cage steric hindrance.

From a general point of view, these hybrids show lower melting temperature and melting enthalpy, associated with lower crystallinity with respect to reference polymers [32]. This behaviour is explained by the POSS hindrance in macromolecules arrangement during polymer crystallisation, resulting in smaller and less regular polymer crystals, having lower melting point. Moreover, glass transition temperature is often undetectable [31].

Both polyethylene/POSS and polypropylene/POSS hybrids show a higher thermoxidative stability as compared with reference homopolymers [31, 33], evidenced by the retarded weight loss observed in thermogravimetry.

Acrylate and methacrylate-based POSS copolymers were widely studied after the pioneer work by Lichtenhan *et al.* [35] reporting homo- and copolymerisation of monomethacryl functionalised POSS by free radical polymerisation. The incorporation of methacrylate POSS monomer units into methacrylate polymers causes significant changes in the copolymer properties. As an example, the glass transition temperature for POSS methacrylate/butyl methacrylate copolymer containing 10%mol of cyclopentyl substituted methacrylate POSS is 130°C higher than the reference polybutylmethacrylate (T_g=20°C) [35]. The effect of different R substituents on monomethacryl POSS/methyl methacrylate copolymers was studied with R=isobutyl, isoctyl or phenyl, with methacrylate POSS content from 0 to 100% [36]. The copolymerisation with isobutyl methacrylate POSS does not strongly affect T_g as compared with neat PMMA, whereas significant effects are obtained with both isoctyl methacylate POSS and phenyl methacrylate POSS. In particular, copolymers containing phenyl POSS show a dramatic T_g increase (*ca.* +110°C at 50%wt. POSS), whereas isoctyl moieties induce a lower glass transition temperature (*ca.* -80°C at 50%wt. POSS). Acrylate and methacrylate POSS copolymers were also prepared by atom transfer radical polymerisation (ATRP) to obtain tailorable block copolymers [37-40]. The use of acrylate and methacylate POSS copolymers was proposed for curable dental resins, thanks to their higher strength, improved wear resistance and low volumetric shrinkage during curing [41-43]. The preparation of PMMA/POSS nanocomposites by melt blending was also studied, in comparison with correspondent copolymers, evidencing low POSS solubility and formation of crystallites in addition of a limited nanodispersed fraction [44]. Blends of PMMA with acrylic POSS showing miscibility up to 10%wt. were analyzed to determine the effect of well-dispersed POSS nanoparticles on the thermomechanical properties, evidencing a plasticizing effect [45].

Few works have been also reported on the preparation of polyolefin-based POSS nanocomposites. Fu *et al.* [46] reported the first study concerning PP/POSS composites evaluating their crystallisation behaviour, under quiescent and shear states. Octamethyl-POSS was added by melt blending in an internal mixer to PP at quite large concentrations (10, 20 and 30%wt.) and the crystallisation behaviour was studied by means of DSC and in-situ SAXS measurements. POSS was found to influence quiescent melt crystallisation enhancing (by acting as a nucleating agent) or retarding the crystallisation process, depending on its concentration. Whereas, under shear, the POSS always accelerated such mechanism. More recently, the same research group investigated the physical gelation in ethylene-propylene (EP) copolymer melts induced by POSS molecules [47]. EP/octamethyl-POSS composites were prepared by melt-mixing in a twin-screw microcompounder with EP copolymers characterised by different ethylene contents and varying the POSS loadings from 10 to 30%wt. From XRD analysis it was found that no molecular dispersion of POSS cages could be achieved as 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 and the glass transition temperature (T_g) value (both calculated by means of DMA analysis) as compared to neat EP. The non-isothermal crystallisation of HDPE/POSS nanocomposites was recently studied by Joshi *et al.* [48]: the crystallinity of HDPE was found to be dependent on the amount of added octamethyl-POSS and on the cooling rates.

The first research work on styrenics/POSS hybrid was reported in 1996 by Haddad and Lichtenhan, with the preparation of 4-methyl styrene/styrylethyl-POSS copolymers by free radical polymerisation [49]. POSS drastically affected the thermal properties of PS, in particular modifying glass transition and degradation onset temperatures. Viscoelastic behaviour of 4-methyl styrene/styrylethyl-POSS copolymers has been deeply studied, showing a rubber-like behaviour at high temperatures, depending on the R groups on POSS (either cyclopentyl and cyclohexyl) [50]. Styrene/styrylethyl-POSS copolymers were also prepared with different R groups on POSS (isobutyl, cyclopentyl, cyclohexyl) and characterised by dynamic mechanical analysis, showing increased storage modulus at high temperature [51]. The effect of POSS cage size (T_8, T_{10}, T_{12}) and of R group on POSS was recently studied in PS/POSS copolymers by means of molecular dynamics simulations [52]. Significant increase on both glass transition temperature and elastic modulus were predicted with phenyl substituted POSS, whereas limited or no effect are predicted with alkyl groups, due to lower compatibility with PS aromatic rings resulting in a less efficient molecular packing. The preparation of PS/POSS nanocomposites by melt blending have been also preliminary explored, showing the possibility to obtain submicron POSS dispersion, depending on POSS organic substituents [53].

From the above brief review of the results reported in literature, three are the most promising application fields for POSS-based nanocomposites and hybrids: fire retardancy, selective permeability and glass transition temperature tailoring. In the last years, many efforts have been dedicated to the development of halogen free flame retardants for polymers; in this field, attention is given to silicon containing flame retardants such as silanes, siloxanes and silsesquioxanes [54,55]. These compounds are recognised to be 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 [56,57]. In PP a 40% reduction on 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 layer, 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. The same barrier effect has been proposed for POSS nanocomposites, resulting from accumulation of a ceramic protective layer produced by POSS degradation during the early stage of combustion [9]. 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 the nanocomposite surface during UL94 tests [58], leading to V0 classification, whereas neat PPE was classified V1 [59]. Bourbigot *et al.* prepared polyurethane/POSS (TPU-POSS) nanocomposites coatings for textiles and tested knitted multifilament yarns by means of a cone calorimeter apparatus. The use of TPU-POSS coating on polyester woven fabrics resulted in a significant reduction of the heat release rate peak (up to 50%), in particular with the use of phenyl-T_{12} POSS and of polyvinyl silsesquioxane resin, whereas methyl-T_8 POSS was found to be almost ineffective [60,61]. The same research group also prepared multifilament yarn knitted fabric with PP/polyvinyl silsesquioxane resin nanocomposites, showing an increase of the time to ignition with no significant effects on the heat release rate [61]. 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 [62]. Synergic formulations with phosphorous-based fire retardants were recently studied in vinyl esters thermosets nanocomposites [63]. 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.

Polymeric membranes are often produced with multi phase materials, including silsesquioxanes nanocomposites and hybrids [64]. The basic idea for the use of silsesquioxane is to take advantage from the porosity obtained tailoring the Si-O framework in regular structures of ladder-like silsesquioxane and POSS. As an example, POSS can be organised in a supramolecular structure with tuneable porosity by crosslinking cages to obtain the architecture designed for a specific application depending on the length of the bridging agent chain. POSS copolymers and polydimethylsiloxane-based POSS nanocomposites were used to prepare membranes for water-ethanol separation [65], trying to find a solution cheaper than zeolites. Despite the high flux obtained, a very limited selectivity was obtained with POSS-based materials, namely due to free volume at the POSS-polymer interphase [66]. Dealing with oxygen and nitrogen separation, the use of intercage POSS porosity has been taking into consideration, in particular with T_{12} and T_{14} cages, whereas T_8 cubic cage appears to be too small to allow the transport of both oxygen and nitrogen [66,67].

As discussed above for some specific cases, the addition of POSS, even at low concentration, can induce significant modifications in the glass transition temperature (T_g) as compared with the neat polymer. Increased or lowered T_g values can be obtained, mainly depending on the POSS organic substituents R; in general, with small or rigid R groups an increased T_g value is observed, whereas lower values correspond to longer substituent chains. This is explained by the different free volume associated to the organic substituents: long and flexible chains increase free volume, thus allowing a higher macromolecule mobility, whereas shorter substituents makes POSS behave like rigid inclusions, hindering polymer chain motion. The simplest model to explain the increase of temperature necessary to allow macromolecules flow is based on the hindrance brought by POSS cages dispersed into the matrix; in fact, if polymer chains find an obstacle during their flow, an energy surplus is required, resulting in a higher transition temperature. Some authors explain the T_g behaviour of POSS-based hybrids with the reptation with sticky points model [50]. Nevertheless, in the case of materials containing POSS nanocrystals and in semicrystalline polymers, this model seems to be insufficient to explain the obtained properties and other interactions involving POSS nanocrystals and polymer crystallinity are to be taken into account. In the field of functional materials, the possibility to tailor glass transition temperature is of great interest, allowing to expand the temperature range for their application. Particularly significant is the opportunity to increase T_g, which is usually difficult with traditional additives.

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Polymer nanocomposites by reactive blending

An extensively used approach for preparing nanocomposites is the sol-gel-technique which allows the formation of metal oxide frameworks. The sol-gel process [1] based upon hydrolysis-condensation reactions of the metal alkoxide leads to an inorganic network that causes the precipitation and dispersion of inorganic fillers throughout the polymer matrix. From the literature, two types of organic-inorganic materials produced by sol-gel process are considered. In the first type, there is no covalent bonding between organic and inorganic phases but mainly hydrogen bonding between both organic and inorganic phases. Generally, these organic-inorganic materials are elaborated by mixing an organic polymer with a metal alkoxide such as tetraalkoxysilane in the presence of a solvent [2-5]. The word of nanocomposites seems to be more appropriate for such materials because they behave as thermoplastics filled with inorganic domains. The second class of materials are organic-inorganic hybrids materials with the existence of covalent bonds between polymer matrix and inorganic phase. Hybrids systems prepared by sol-gel process can be obtained using different synthetic approaches, the most common one being the hydrolysis-condensation reactions of alkoxysilanes in the presence of alkoxysilane prefunctionalized polymers (Fig. 1) [6-8].

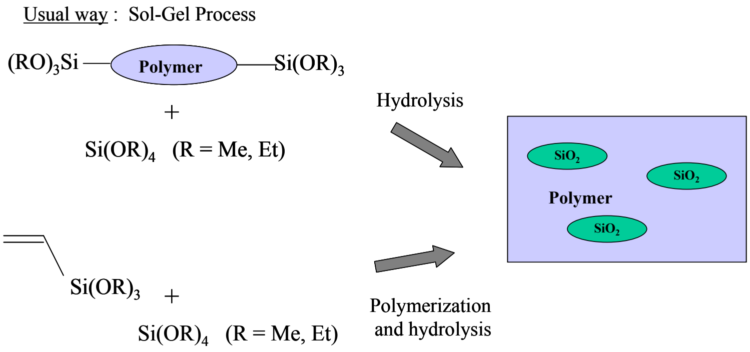

Figure 1: Principle of synthesis for organic-inorganic hybrid materials

From a processing point of view, these materials behave as thermoset polymers. However, a major problem associated with the sol-gel process is the use of organic solvent which limits the application to coating of glass, metal and polymer substrata. For example, Sengupta et *al*. [9] synthesized Polyamide 6.6/silica nanocomposite through the in situ hydrolysis-condensation reactions of tetraethoxysilane (TEOS) in the presence of PA 6.6 dissolved in formic acid. Sometimes modifier such as glycidoxypropyltrimethoxysilane can be added during the in situ polymerization leading to homogeneous dispersion of silica in the PA66 matrix [10]. Polyurethane/silica are obtained from aqueous emulsions of cationic polyurethane ionomers mixed with TEOS [11]. Polyacrylamide are also prepared from acrylamide emulsion in presence of silica [12]. Similarly Grandi et al [13] prepared PEG/silica nanocomposite from TEOS and a solution of PEG. Others types of fillers cab be created through the same approach. For example, titanate phased is generated from titanium butoxide hydrolysis-condensation reactions in surlyn ionomer [14]. However, nanocomposites with extensively used polyolefin, like polypropylene and polyethylene, have not been prepared for their poor solubility in common solvents at room temperature. Consequently and despite many efforts in the past, the conventional routes for preparing such nanocomposites have their deficiencies and could not be exploited. In order to face this challenge, extensive studies have been devoted to polymer-layered silicate nanocomposites by molten processing methods. However, the successful synthesis of polyolefin nanocomposites requires the use of maleated polyolefin and surfactant intercalated clay to improve the poor compatibility between non polar polymer and clays [15-17]. Nevertheless, limited improvements of mechanical or barrier properties were generally achieved.

On the other hand, sol-gel methods were used to prepare silica/rubber nanocomposites or silica reinforced rubber vulcanizates in order to overcome the conventional mixing in usual processing techniques. As for example, the *in situ* loading using the sol-gel reaction of TEOS has been developed to reinforce the rubber vulcanizates. From a general preparation point of view, the rubber vulcanizates are swollen in TEOS and soaked in an aqueous solution. The reaction of TEOS takes place in two steps, the hydrolysis and the condensation reaction, to produce SiO_2. This sol-gel process has been reported for the preparation of nanocomposites based silicone rubber [18, 19], polyisobutylene [20], several diene rubbers [21-26] and more recently in acrylic and epoxidized natural rubber [27]. In addition, Kohjya *et al*. [28] and Murakami *et al*. [29] proposed an alternative practical preparation method of *in situ* silica loading in the rubber matrix. The sol-gel reaction of TEOS produced the silica nano-particles in the unvulcanized rubber matrix and the *in situ* silica filled rubber compound was then subjected to the mixing and heat processing to prepare rubber vulcanizates. Nevertheless, this method can be developed to amorphous polymers only such as rubbers and elastomers.

More recently, Sun et *al*. [30] report on polypropylene/silica nanocomposites prepared by two steps: TEOS is first impregnated into PP matrix using supercritical carbon dioxide (SC CO_2) as a swelling agent and carrier followed by hydrolysis/condensation reaction of TEOS confined in polymer network. The results showed that nano-sized silica networks were formed and distributed uniformly in PP matrix. In addition some polymer molecules might entangles with the silica networks. Jain *et al*. [31] developed a new route by combining solid-state modification by grafting vinyl triethoxysilane (VTEOS) with a sol-gel method. Following this, they prepared PP/silica nanocomposites with varying degree of adhesion between silica nano-filler and matrix. In a previous study [32], the group of CNRS-IMP presented a new route to elaborate organic-inorganic hybrids materials. This method is based upon two successive steps. The first one is the crosslinking of polymer which contains pendant ester groups such as poly(ethylene-co-vinyl acetate) (EVA) through ester-alkoxysilane interchange reaction in molten state. The subsequent step is the hydrolysis-condensation reactions of available alkoxysilane groups in the polymer network leading to the silica network co-grafted onto the organic network (Fig. 2) [33].

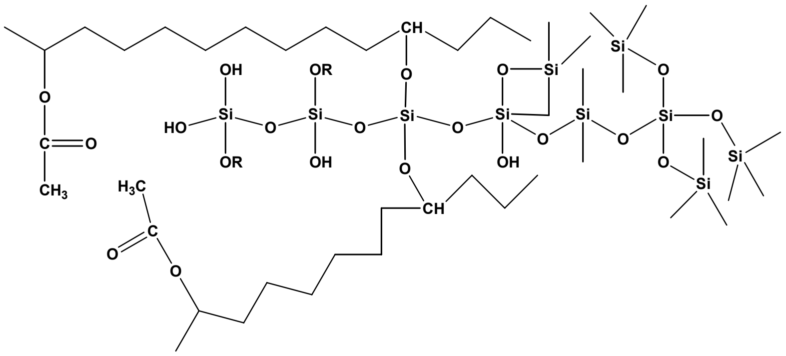

Figure 2: Final structure of organic-inorganic hybrid material

The main advantage of this original is to achieve organic-inorganic hybrid materials in molten state without the presence of solvent. Moreover, this method can be integrated into processing operations of thermoplastic such as extrusion (Fig. 3) [34]. Then, it offers the possibility to tailor articles made of organic-inorganic hybrids in bulk.

The immediate consequence of the results, which we obtained on organic-inorganic hybrid materials, was to consider this «sol-gel» synthesis within thermoplastic polymers during their processing in a medium of high viscosity.

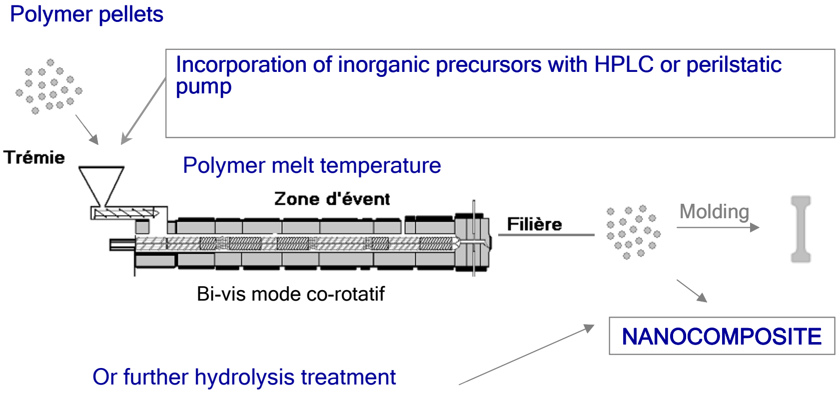

Figure 3: Principle of in situ synthesis of nanocomposite by reactive extrusion

The fundamental difference with the hybrids lies in the fact that a nanocomposite synthesized by in situ generation of filler can be reprocessed contrary to hybrid material. The benefit of this synthesis in medium of high viscosity should limit mobility of the elementary particles and consequently the processes of agglomeration.

This new concept was validated by the control of hydrolysis-condensation reactions of tetraalkoxysilane dispersed during processing of polar and apolar molten polymers. Respectively domains of silica of diameter about 25 and 50nm were obtained (Fig. 4).

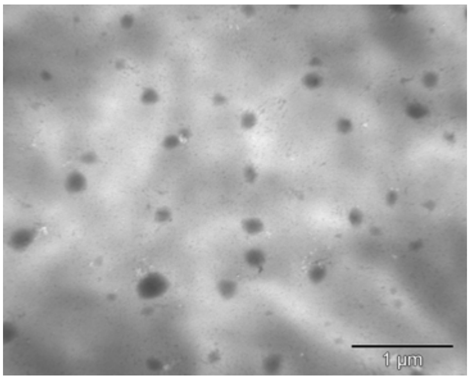

Figure 4: MET of alumina/Polar polymer obtained by sol-gel reactions without solvent

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