Polymer/polyhedral oligomeric silsesquioxanes (POSS) nanocomposites

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1. Elaborate a literar study focused mainly on the following two points:
1.1. Preparation and properties of polyhedral oligomeric silsesquioxanes.
1.2. Main characteristics of polymer/polyhedral oligomeric silsesquioxanes nanocomposites.
2. Compare the usage of this nanofiles in different polymer matrixes.
3. Elaborate a short overall summary of the advantages and disadvantages of POSS nanofillers.

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ABSTRACT IN CZECH

Cílem této bakalářské práce bylo shrnutí informací o sloučenině POSS (Polymer Oligomeric Silsesquioxanes) Nejprve byla věnována pozornost historii POSSu a způsobu jeho přípravy. Příprava POSSu má dvě části, nekompletní a kompletní kondenzaci. POSS může být modifikován dalšími sloučeninami. Tyto modifikace podstatně ovlivňují vlastnosti. V této práci byly popsány modifikace kovy, nízkomolekulárními sloučeninami, vysokomolekulárníni sloučeninami a polymerem.

Klíčová slova: POSS, Polymer Oligomeric Silsesquioxanes, kompletní a nekompletní kondenzace

ABSTRACT

The aim of this Bachelor thesis was the summary of information POSS (Polymer Oligomeric Silsesquioxanes) compound. Firstly, the attention was paid to the POSS history and the way of POSS preparation. The POSS preparation have two sections, incompletely and completely condensation. POSS can be modified with other compounds. This modification substantially influences POSS attributes. In this thesis POSS modification with metal, low molecular compounds, high molecular compounds and polymer are described.

Keywords: POSS, Polymer Oligomeric Silsesquioxanes, completely and incompletely condenzation

Tímto bych si dovolil poděkovat vedoucí mé bakalářské práce Ing. Lucii Kovářové Ph.D. za odborné vedení, poskytování cenných rad a informací k tématu.

Souhlasím s tím, že s výsledky mé práce může být naloženo podle uvážení vedoucího bakalářské práce a ředitele ústavu. V případě publikace budu uveden jako spoluautor.

Prohlašuji, že jsem na celé bakalářské práci pracoval samostatně a použitou literaturu jsem citoval.

Ve Zlíně, 05. 06. 2006 .....

podpis

OBSAH

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INTRODUCTION

Si-O bond is stronger than the Si-H bond and much more than the Si-Si bond. As a result, Si-O-Si-O-Si chains make up the skeleton of the silicate chemistry. Extensive studies about conversions processes by using ion irradiation of polymeric and alkoxide precursors with different C/Si and O/Si ratios was performed by Pivin and Colombo [1] in order to obtain Si-O-C bonds. The Si–O–C films were produced from polysiloxanes and polycarbosilanes.

A silicate skeleton can also occur in the form of cages, where the structure is based on Si–O linkages with a silicon atom at each vertex. Each silicon vertex can accept substituents and the nature of the external cage substituent determines its physical and chemical properties. The cage compounds $(RSiO_{1.5})_n$, where R is an organic or inorganic group with n=6, 8, 10 or 12, are a versatile class of building blocks units for the synthesis of new materials. Cage structures connected together in a finite 3-D molecular skeleton are known as polyhedral oligomeric silsesquioxanes (POSS). These POSS materials are also referred to belong to the class of spin-on-glasses (SOG) materials.

A very interesting application for the new based Si–O materials is in the semiconductor industry, as low dielectric constant (k) materials. Purely organic materials do not present mechanical and thermal stability and do not support elevated processing temperatures and the high stresses in the interconnect structure. Consequently, there are great interests in organic/inorganic hybrids, with a rigid Si–O network allied to a low k characteristic of polymeric substances [2].

I. THEORETICAL PART

1 POSS HISTORY

Articles on the synthesis, structure and properties of silsesquioxane resins have been published before the 1940s. However two landmark publications pertaining to well-defined POSS structures were the 1946 Scott [3] paper on completely condensed POSS cages, and the incompletely condensed POSS ‘triol' characterization by Scott and Brown and Vogt [4]. It was not until 20 years later that Feher initiated a research program focused on exploiting the unique geometry and functionality of these silicon–oxygen frameworks. Feher's initial programs were aimed at the modeling of silica surfaces and development of homogenous catalysts, but his group also played a significant role later on in the development of POSS-polymers. So, POSS-polymers are only dated back to 1991.

In 1991, Lichtenhan and the Air Force Research Laboratory received funding from the Air Force Office of Scientific Research (AFOSR) for his proposed development of POSS macromers containing a polymerizable functional group and the subsequent synthesis of a POSS-copolymer [5]. The University-Government collaboration between Lichtenhan and Feher rapidly expanded to include more academic collaborators including Laine and Sellinger [6], Mather et al. [7] and others who were all intrigued by the physical and mechanical property improvements imparted by incorporation of these nanostructured materials into polymer systems. In the late nineties not only was government and academic interest growing, but also that of the industrial sector which desired lowers costs and larger quantities of the material.

The fall of 1998 marked the start-up of Hybrid Plastics in Fountain Valley, CA, which transitioned the government scale-up facilities to the commercial sector through a cooperative research and development agreement. In addition, the award of a 3 year multi-million dollar NIST Advanced Technology Program grant in 1998 to Hybrid Plastics was critical in both reducing the prices of the POSS feedstocks and macromers and increasing production to satisfy the more than 100 companies now investigating how the incorporation of POSS improves material properties for their applications. In the summer of 2003, Hybrid Plastics launched critical agreements with Southern Mississippi State University and the City of Hattiesburg for their development of a 26,000 sq ft production facility and a 1500 sq ft R&D center.

The nearly exponential increase in the number of academic researchers, academic publications, government programs, and industrial research efforts on POSS nanostructured chemicals has made it one of the top nanomaterials in the nanoscience/nanotechnology field. Indeed, the versatility of the POSS molecule, the more than one hundred demonstrated compatible polymer systems and the innumerable applications makes it difficult to understand and discern the current and future direction. However, it is clear to the author that at least one concerted effort with a single-minded goal of predicting and controlling structure–property relationships is needed, and is being pursued by a number of research groups working with POSS nanostructured chemicals.

1.1 Preparation

POSS was firstly synthesised in 1946 by chemist Scott W. Donald. They worked on thermal rearrangement of branched-chain methylpolysiloxanes and their results were completely condensed POSS cages. They prepared siloxanes on this way:

A mixture of 6 l H_2O (water), 1200 g. BuOH (butanol), and 600 g PhMe (phenylmethyl), was treated with 830 g Me_2SiCl_2 (dimethyldichlorsilane), and 970 g $MeSiCl_3$ (methyltrichlorsilane) in 600 g PhMe with vigorous stirring. The organic layer was washed free of acid, the BuOH and PhMe was distilled in vacuo, and the residue heated at 350-600°C, during which thermal rearrangement occurs, gives approximately 66% of volatile material. Distillation and crystallization (usually from PhMe) give about 1% each of the following fractions: $Me_8Si_5O_6$, boiling point 203°C, melting point 118°C; $Me_{10}Si_6O_7$, bp 232°, mp 51°C; $Me_8Si_6O_8$, bp 220°C, mp 119°C; $Me_{10}Si_7O_9$, bp 248°C, mp 150°C, $Me_{10}Si_8O_{11}$, bp 257°C, mp 139°C; $[MeSiO_{1,5}]_{2n}$, sublimes without melting.

Me_2SiCl_2 (1425 g) and 375 g $SiCl_4$ in 600cm^3 PhMe, added to 1200 g BuOH, 600 g PhMe, and 6 l H_2O, give less than 1% of $Me_8Si_5O_6$, bp 204°C, mp 121°C, and $Me_{10}Si_6O_7$, bp 234°C, mp 57°C; about 7% of $Me_{12}Si_7O_8$, bp 254°C, mp 31°C. These structures were assigned on the basis that the Si-O bonds alone were involved in the rearrangement, the methyl groups remaining attached to the Si atoms [8].

Even though the first synthesis of these structures can be traced back in the 1950s, only in the past 10 years POSS have attracted wide-spread interest mainly as precursors to hybrid inorganic/organic materials [9].

At these days polyhedral oligomeric silsesquioxanes (POSS) are usually produced by hydrolytic condensation of trifunctional monomers $RSiX_3$ (see Figure 1 and 2), where X is a highly reactive substituent, such as Cl or alkoxy (see Figure 1)

$$\mathbf{RSiX_3} \xrightarrow{H_2O+solvent} \mathbf{[RSiO_{3/2}]_n}$$

Figure 1. Hydrolytic condensation of trifunctional monomers.

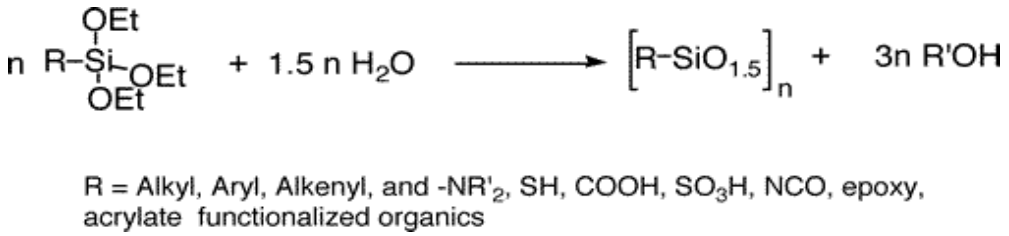


Figure 2. Hydrolysis and condensation of bridged organotrialkoxysilanes

The possibility of producing an ordered array of POSS domains has been studied by Schiraldi et al. [10], Feher et al. [11] and the others.

1.1.1 POSS hydrolytic condensation

Hydrolytic condensation of trifunctional silanes is the main reaction for preparation of silsesquioxanes $(RSiO_{1.5})_n$.– basic unit of POSS. Reaction starting from $RSiX_3$, where R is a chemically stable organic substituent and X is a reactive substituent. Typical functional groups that may be hydrolyzed / condensed include alkoxy- or chlorosilanes, silanols, and silanolates. The large scale synthesis of a wide range of these molecular spherosilicates has become accessible because of the development of new synthetic procedures. When R is a (cyclo) alkyl unit, the POSS-compounds are very soluble in a range of organic solvents (e.g. tetrahydrofuran, toluene, dichlormethan, hexane, ethyleneoxid), and show good

stability in acidic and moderate stability in basic reaction media. The example of POSS hydrolytic condensation using tetrahydrofuran solvent can be seen in Figure 3.

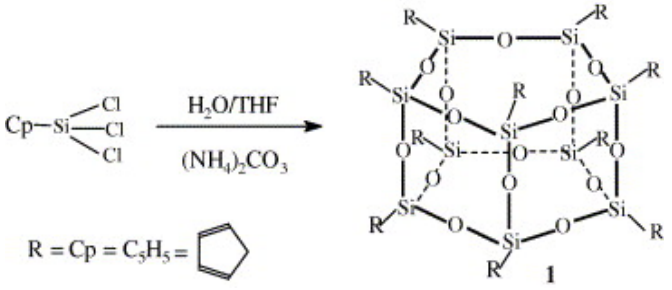


Figure 3. Preparation of $Cp_{10}Si_{10}O_{15}$ (1) oligosilsesquioxane

Many parameters influence the hydrolytic condensation and determine which silsesquioxane species are formed and in which amounts. Synthetic methodologies that combine pH control of hydrolysis / condensation kinetics, surfactant-mediated polymer growth, and molecular templating mechanisms have been employed to control molecular scale regularity as well as external morphology in the resulting inorganic/organic hybrids (from transparent nanocomposites, to mesoporous networks, to highly porous and periodic organosilica crystallites) all of which have the silsesquioxane (or $RSiO_{1.5}$) stoichiometry.

Reactions of trifunctional organosilicon monomers show Figure 4.

$$nRSi(OH)_3 \xrightarrow{-(xH_2O)} [nSiO_{3/2}]_n\,(H_2O)_{3n/2-x} \xrightarrow{(3n/2-x)H_2O} [RSiO_{3/2}]_n$$

Figure 4. Reaction of trifunctional monomers with incompletely and completely POSS

This reaction has two steps. The first step is incompletely condensed POSS* $[nSiO_{3/2}]_n(H_2O)_{3n/2-x}$ and the second step is fully condensed POSS*$[RSiO_{3/2}]_n$

1.1.1.1 Incompletely condensed POSS - $[nSiO_{3/2}]_n$ $(H2O)_{3n/2-x}$

POSS silanols are incompletely condensed frameworks possessing a hybrid inorganic–organic, three-dimensional structure and containing one–to–four silanol (Si-OH) groups. Unlike most other silanols that are generated in situ, the POSS silanols are stable towards condensation. The Si-OH groups in the POSS silanols are reactive enough to allow a wide range of applications; their chemistry has been extensively developed over the past 10-15 years. An example of their reactions is illustrated below in Figure 5. When trisilanol is reacted with a variety of group 14 compounds of the type RMX_3 (R = alkyl, alkenyl, aryl, H; M = Si, Ge, or Sn; X = halogen or alkoxide), a wide variety of monomeric T_8 silsequioxanes results.

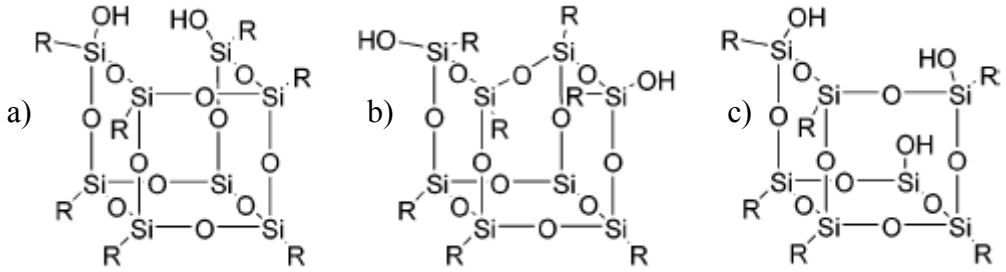


Figure 5. Incomplletely condensed cluster structures:
a)$T_8(OH)_2$ - regular exo, b) $T_8(OH)_2$ – Z-exo, c) $T_7(OH)_3$

1.1.1.2 Fully condensed POSS - $[RSiO_{3/2}]_n$

The fully condensed silsesquioxane cages $[RSiO_{3/2}]_n$ surrounded by nonreactive organic groups permit the robust, inorganic, Si-O core to be compatible with an organic matrix. Thus, they may be compounded with traditional plastics yielding true nanocomposites with molecular-level dispersion. Careful hydrolysis leads to well-defined, fully condensed, prismatic, POSS structures T_8^R, T_{10}^R, T_{12}^R (see Figure 6).

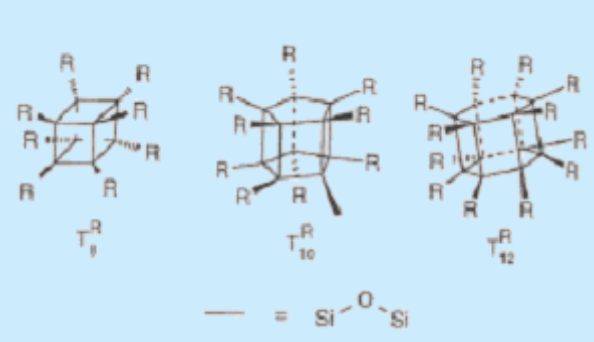
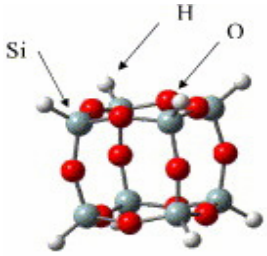


Figure 6. Diagram showing the fully condensed and prismatic POSS structures, T_8^R, T_{10}^R, T_{12}^R, following the hydrolysis process.

1.2 Structure

POSS is a cage-like silsesquioxane, the basic unit, with an inner inorganic silicone $(SiO_{1.5})_n$ framework in which eight organic groups can be appended. The word *siloxane* is derived from the words **Sil**icon, **ox**ygen, and alk**ane**. In other words, each silicon atom is bound to an averange of one and a half (sesqui) oxygen atoms and to one hydrocarbon group (ane). An example of silsesoxanes structure is ilustrated in Figure 7 and 8. Silsesquioxane makes a bridge between two component classes of materials. The number of functional groups in the POSS molecule decides about the structure generated. POSS particles have diameters from 1 to 3 nm and are considered to be the smallest possible particles of silica.

a)



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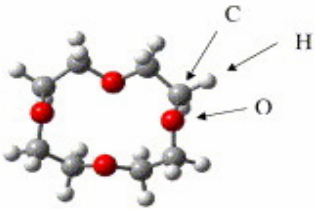


Figure 7. General structure of one POSS unit, red particles - oxygen atoms, white - hydrogen and grey particles - silicon
a)view from the side to POSS unit, b) view from top to POSS unit..

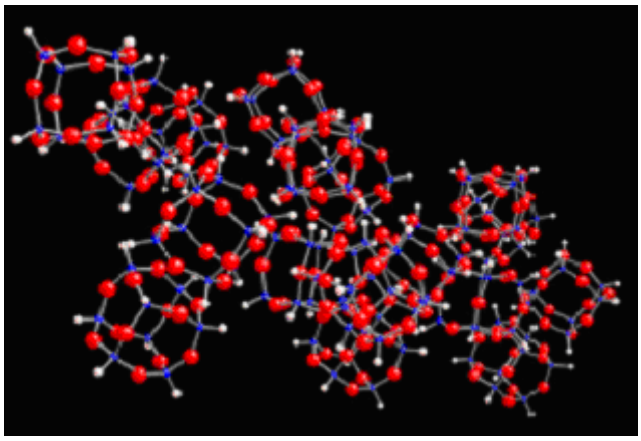


Figure 8. Three dimensional POSS structure
Red particles are oxygen atoms, white particles are hydrogen atoms and blue particles are silicon atoms.

Resultant nanostructuration is depent on different processes, ideal molecular dispersion multifunctional POSS unit. Very important is the self-assembly of organic groups (Figure 9).

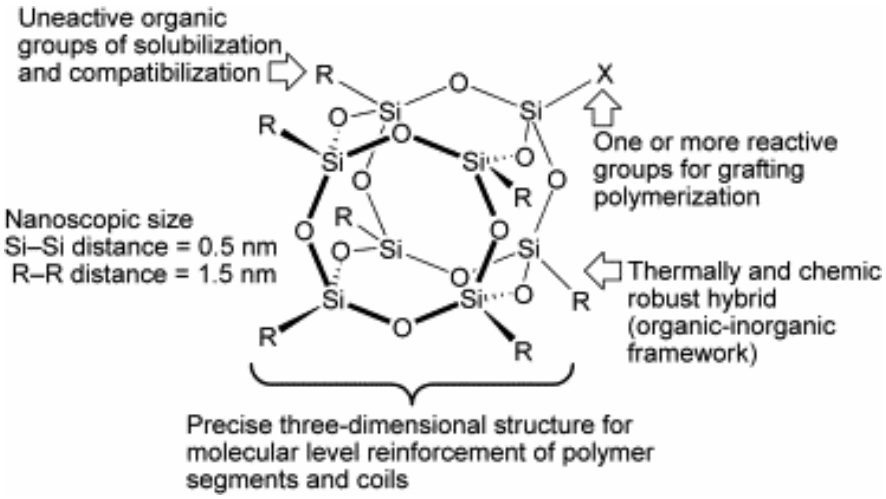


Figure 9. Main characteristic and dimension of POSS

1.3 Polymer POSS

POSS monomers can be polymerized or grafted using standard techniques to yield inorganic-organic hybrid homopolymers and copolymers. In a polymer structure is monofunctional POSS incorporated as pendant unit. Multifunctional POSS is in a polymer network as crosslinking sites.

Ideal description of the polymer structure is very complicated. Description is depending on separation of inorganic and organic parts either initially or in the course of polymerization. A broad range of POSS aggregates with size varying is depending on the kinetics of phase separation and polymerization.

$RSiX_3$ monomers (R=alkoxy, halide) oligomerize under typical sol-gel conditions to form polyhedral oligosilsesquioxanes, or soluble, randomly linked arrays of polycyclic cages. On the other hand, sol-gel polymerization of a molecular building block that contains an organic fragment attached to two or more trialkoxysilyl groups leads to bridged polysilsesquioxanes.

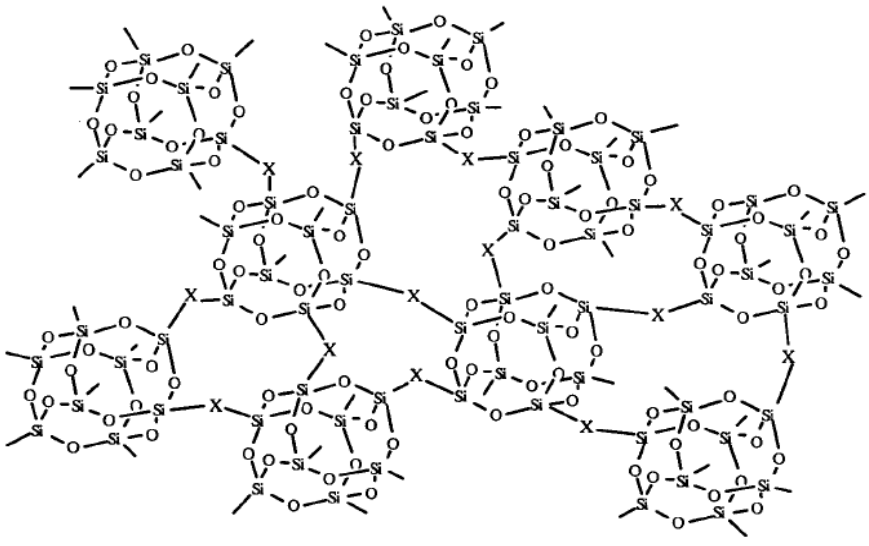


Figure 10. POSS polymers, where X are the bridges.
For example X can be -CH_2-CH_2-

Chemical diversity of POSS structure is very various, because POSS can have many of functional groups (see Figure 11.).

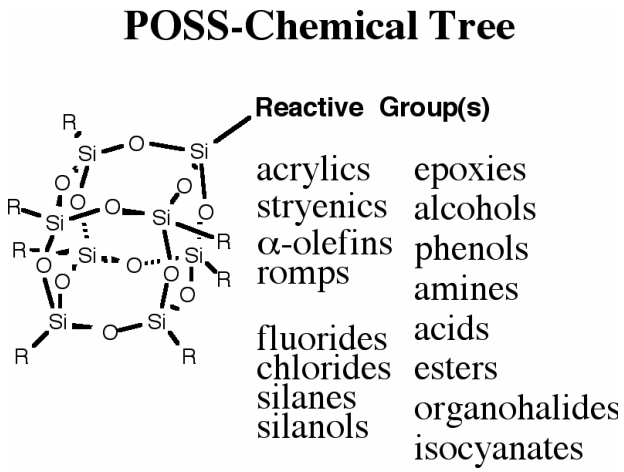


Figure 11. Main reactive groups of POSS

2 THE AIMS OF BACHELOR THESIS

1. The summary of POSS modification with metal.
2. The summary of POSS modification with low molecular compounds.
3. The summary of POSS modification with high molecular compounds.
4. The summary of POSS utilization in polymer matrixes.
5. POSS advantages and disadvantages in practice usage.

II. EXPERIMENTAL PART

2.1 POSS modification

2.2 Metal silsesquioxanes

The resemblance of silsesquioxanes to silica supports is not only apparent from the molecular structure, but the electronic properties of silsesquioxane silanol groups mimic the behavior of silica as well. A few important structural similarites between silsesquioxanes and schematized silica surfaces are depicted in Figure 12.

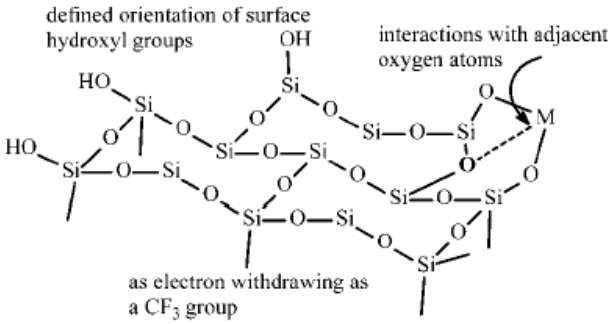


Figure 12. Schematic overview of silica-based catalyst support, indicating important surface properties

First of all, the defined orientation of the silanol groups, which is also present in silsesquioxanes, may ensure a strong multi-dentate bonding to metals. Furthermore silsesquioxanes have enough residual siloxane bridges to resemble the silica surface and these residual siloxane bridges can interact with the metal. Since the discovery of silsesquioxanes rich coordination chemistry has been developed with elements throughout periodic table.

2.2.1 Group 1. (Li, Na, K)

F. J. Feher reported **sodium** complexes as intermediates in the synthesis of transition metal complexes. These intermediates were either not isolated or found to be unstable out of solution. The groups of Aspinall, Edelmann and Abbenhuis have used **lithium silsesquioxanes** extensively as transmetallation agent to prepare transition

metalcomplexes. In some cases lithium ions remain present in the transition or main group metal complex [12].

2.2.2 Group 2 (Be, Mg)

Edelmann et al. [13] published a crystal structure of a mixed **beryllium-lithium silsesquioxane**. Smet et al. reported the use of **magnesium-substituted silsesquioxane** as a intermediate in the reaction with epoxides [14]. Liu [15] reported the application of **magnesium-substituted silsesquioxanes** as model supports for titanium-based alkene polymerization catalysts. Hanssen [16] described the synthesis and reactivity studies of a tetranuclear **magnesium complex**.

2.2.3 Group 3 (Sc, Y, La, Lanthanides and Actinides)

Edelmann et al. [17] displayed a great interest in the synthesis of Group 3 and **lanthanide complexes**. They reported samarium and **scandium complexes** of the isolated silanol silsesquioxane 1 (in Figure 13.), a seven-coordinate ceriumsilsesquioxane and various mixed-metal **lithium-lanthanide complexes**.

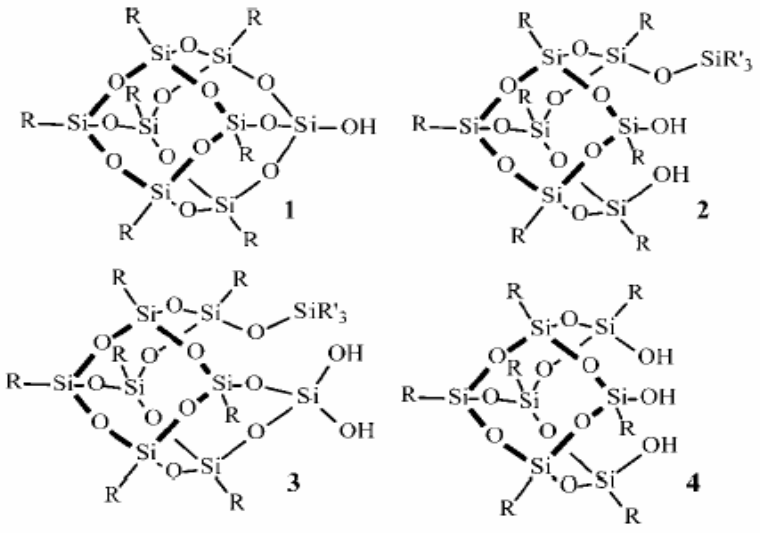


Figure 13. 1 isolated silanol, 2 vicinal disilanol, 3 geminal disilanol, 4 vicinal trisilanol

2.2.4 Group 4 (Ti, Zr, Hf)

H. C. L. Abbenhuis [18] reported the heterogenization of active and selective epoxidation catalysts. Krijnen et al. [19] reported the heterogenization of **titanium silsesquioxane complexes** in mesoporous MCM-41*(Mobile Crystalline Material-is a silicate obtained by a templating mechanism[1,2,3]) type materials (Figure 14). No leaching was observed for all-silica MCM-41 materials, while aluminium-containing MCM-41 had to be silylated after impregnation of the titanium silsesquioxane complex [20].

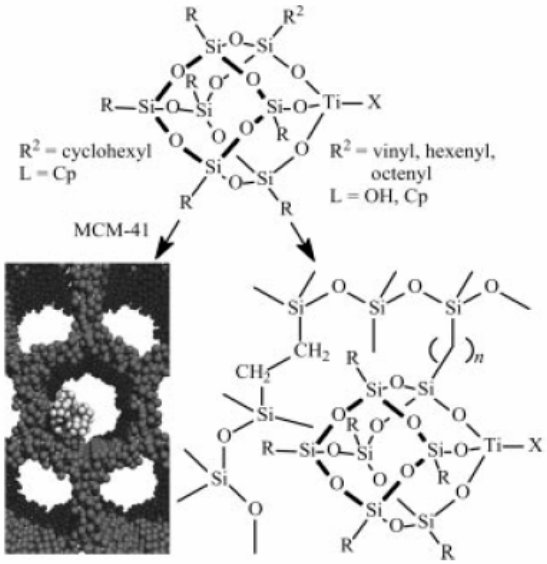


Figure 14. Immobilization of a titanium silsesquioxane complex by physisorption in a mesoporous MCM-41

2.2.5 Group 5 (V, Ta)

Feher et al**.** [21] explored the use of Group 5 metals liganted by silsesquioxanes by reacting vanadium(III) and **vanadium(V) precursors** with silsesquioxane trisilanol compounds (see Figure 15). Wada et al. [22] used **vanadium(V) complexes** to prepare microporous **vanadium silicates** by controlled calcination of the complex in air at 723K.

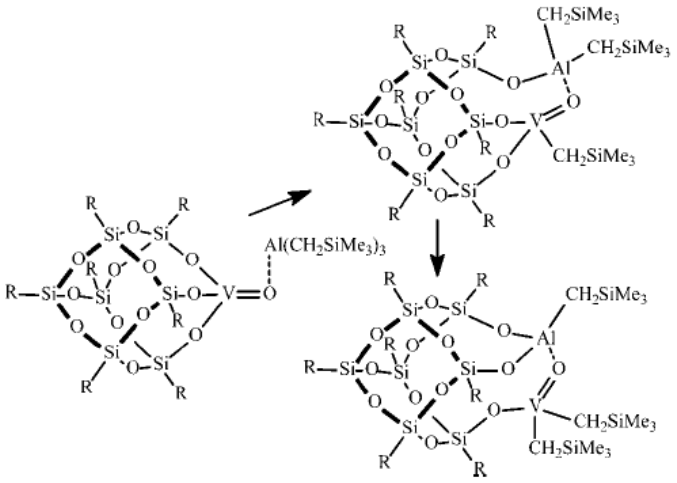


Figure 15. Activation of a vanadium(V) silsesquioxane complex with an alkylaluminium compound

2.2.6 Group 6 (Cr, Mo, W)

These compounds were tested by Feher et al. [23] in the polymerization of ethylene as a surface model for the chromium-based Phillips catalyts. Vorstenbosh et al. [24] employed **chromium silsesquioxane** ester for the catalytic epoxidation of alkenes with tert-butyl hydroperoxide. Maxim et al. [25] used the chromium silsesquioxane for the synthesis of microporous-silica-supported chromium that was foumd to be active in the low temperature catalytic oxidation of ammonia. Smet et al. [26] synthesized a **bis(silsesquioxane)-tungsten complex**, for which the synthesis is atypical as no base is required to trap the HCl formed (Figure 16.).

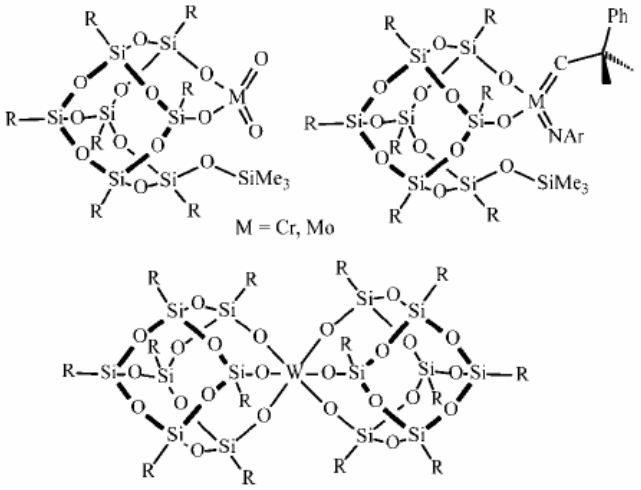


Figure 16. Examples of silsesquioxane group 6 metal complexes

2.2.7 Group 7

No one reported the synthesis of group 7 where is the metal directly linked to the silanol groups. Attempts to synthesize rhenium silsesquioxane complexes resulted in either dehydration reactions of the silsesquioxane, or yielded complicated product mixtures.

2.2.8 Group 8 (Fe, Ru, Os)

In 1990 Liu et al. [27] reported the crystal structure of a **silsesquioxane-substituted osmium cluster**. Marsmann et al. [28] used thiol-functionalized silsesquioxanes to bind to ruthenium and osmium carbonyl clusters. Ott et al. [29] and Edelmann et al. [30] have only reported the synthesis and application of **iron silsesquioxanes** where iron atom is attached to the silanolate groups (see Figure 17).

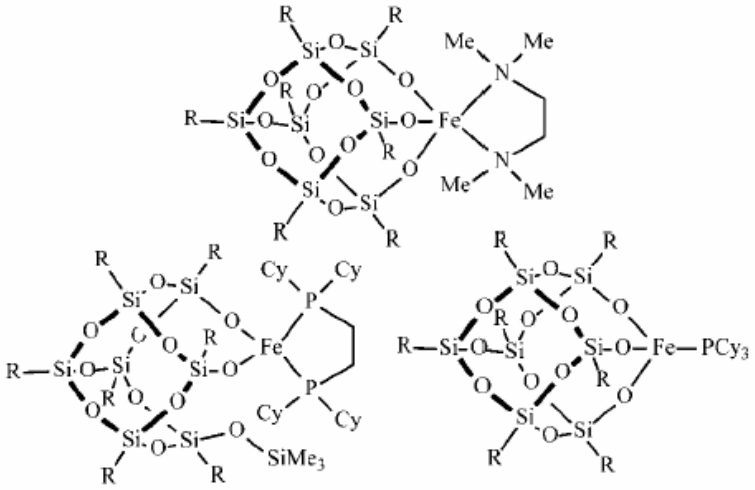


Figure 17. Iron silsesquioxanes reported by Ott et al. and Edelmann et al.

2.2.9 Group 9-10 (Co, Rh, Pt)

Abbenhuis et al. [31] described the reaction of $Pt(CO_3)$(dppe)*N,N-diethyl-2-[4-(phenylmethyl)phenoxy] ethanamine with trisilanol and mono-silylated disilanol silsesquioxane ligands. Feher et al. [32] used mono-silylated thallium silsesuioxide complexes as a transmetallating agent to make **silsesquioxane platinum compounds**, although in some cases the use of thallium silsesquioxide complexes frustrated the synthesis of the complex due to residual thallium ions in the isolated materials.

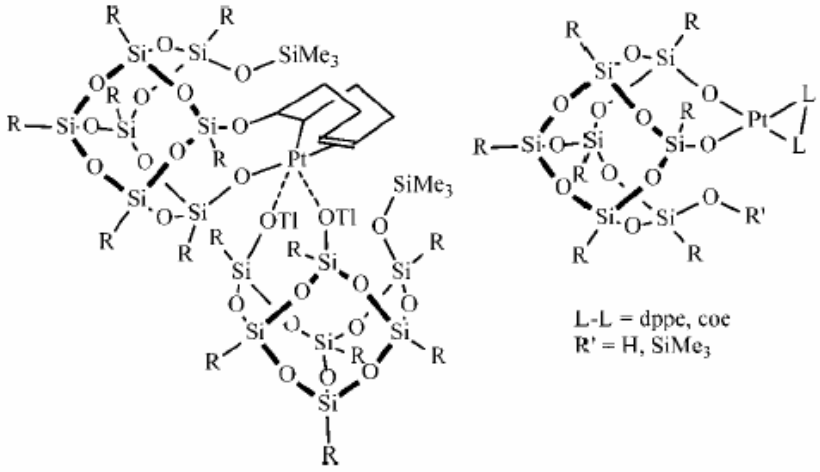


Figure 18. Pt silsesquioxane complexes by Abbenhuis and Feher

Other reported ways of attaching Group 9-10 metals to silsesquioxanes are coordination of a donor group to the metal (S, P) and oxidative addition of a metal to Si-H(Co, Rh). Cole-Hamilton et al. [33] used phosphorous-functionalized silsesquioxane-based dendrimers as ligands for rhodium to perform hydroformylation reactions.

2.2.10 Group 11-12 (Cu, Au, Zn)

Silsesquioxane complex chemistry has not been developed to large extent for metals in these groups. Abis et al. [34] prepared di- and trisubstituted **gold silsesquioxanes** as a model for the interaction of gold carbamate precursors with silica surfaces (see Figure 19.). Pugin et al. [35] used sulfur-functionalized silsesquioxanes as ligands for Au_{55} clusters and were able to correlate the increased Coulomb gap to the increased size of the cluster going from PPh_3 to the silsesquioxanes-based ligand.

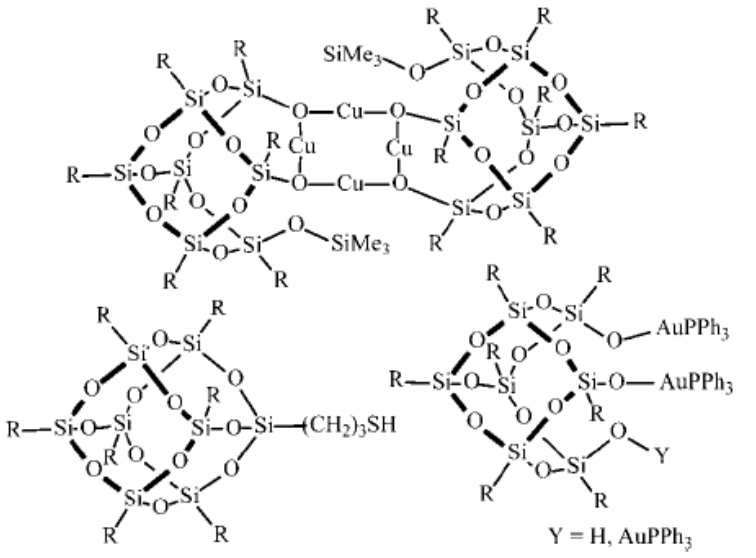


Figure 19. Examples of complexes of copper and gold and thiol-functionalized ligand for gold clusters

2.2.11 Group 13 (B, Al, Ga, Tl)

Feher et al. [36] prepared **aluminum silsesquioxane** complexes as a model for aluminum sites in zeolites and on silica, and as model for methyl alumoxane compounds. Duchateau [37] synthesized **silsesquioxane organoboranes and organoborates** that could be used as models for silica-supported borane activators (Figure 20.). **Thallium silsesquioxane** complexes have been mainly applied for transmetallation reactions where the thallium is replaced by high-valent transition metals.

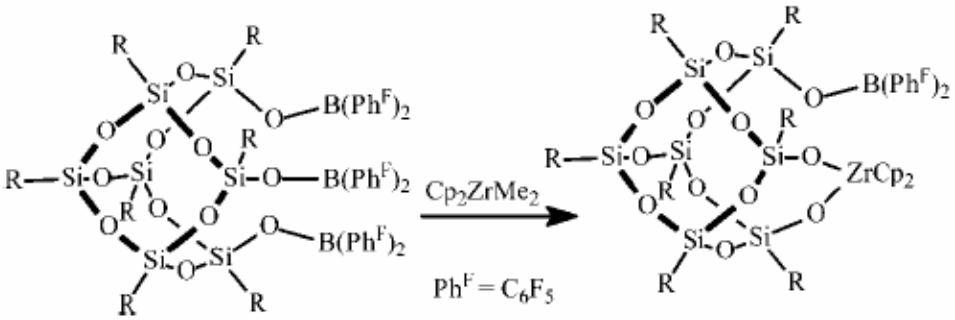


Figure 20. Interaction of dimethylzirconocene with a tris(organobora)silsesquioxane leading to borane-zirconocene exchange

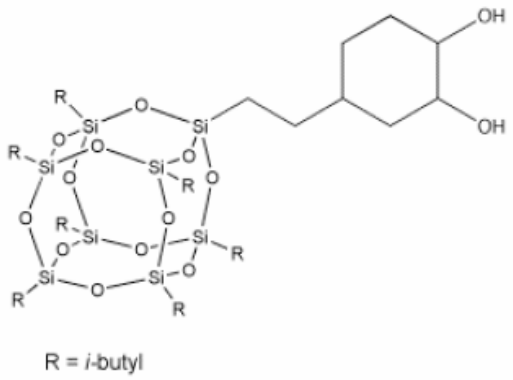
2.3 POSS modification with low molecular compounds

Concerns Hybride Plastics [38] and Sigma-Aldrich [39] modify POSS using low molecular compounds. The POSS modified with these low molecular compunds can be divided to the following categories.

2.3.1 Alcohols and Phenols

This group means that POSS units are modified with alcohol and phenol compounds. One example of this group can be seen in Table 1.

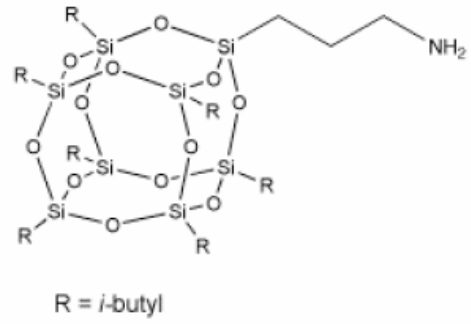
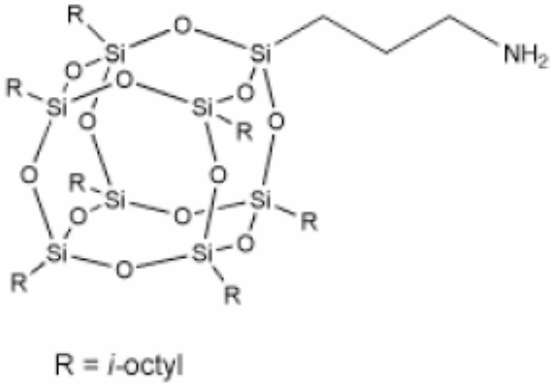
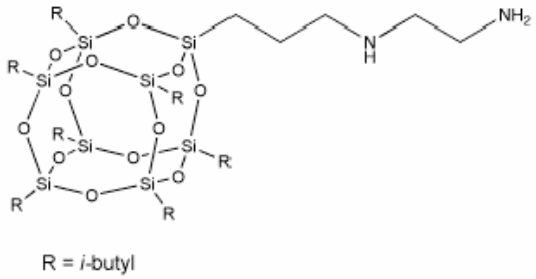
Table 1. Modification POSS with alcohol and phenol compounds

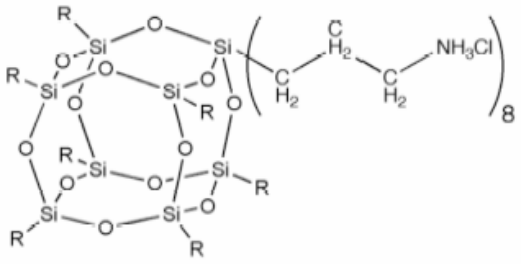
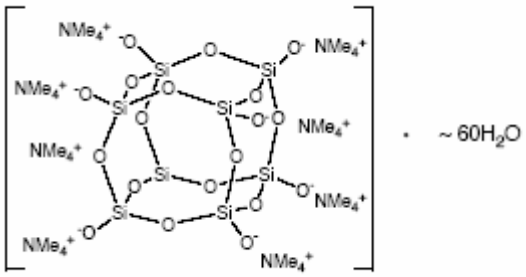
trans-Cyclohexane Diolisobutyl POSS $C_{36}H_{78}O_{14}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform, acetone,hexane **Uses** monomer for condensation, polymerizations to increase strength and toughness	

2.3.2 Amines

This group means that POSS units are modified with amine compounds. The examples of this group can be seen in Table 2.

Table 2. Modification POSS with amine compounds

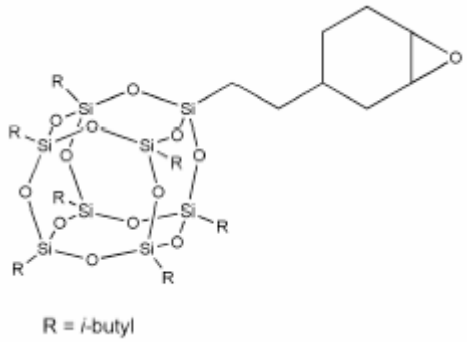
AminopropylIsobutyl POSS $C_{31}H_{71}NO_{12}Si_8$ **Solvent Solubility**: tetrahydrofuran, chloroform **Uses:** grafting agent, chain terminator	
AminopropylIsooctyl POSS $C_{59}H_{127}NO_{12}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform **Uses:** grafting agent, chain terminator, improves hydrophobicity, improves processing	
AminoethylaminopropylIsobutyl POSS $C_{33}H_{76}N_2O_{12}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform **Uses:** grafting agent, chain terminator to improve processing	

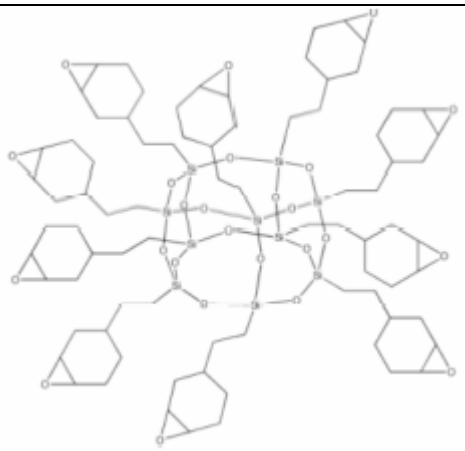
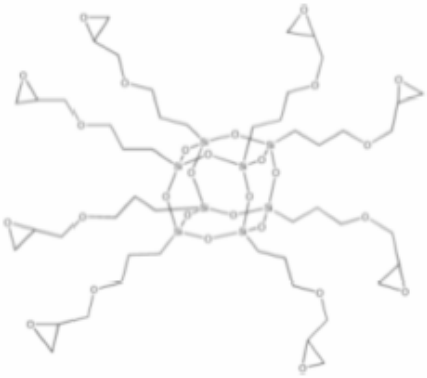
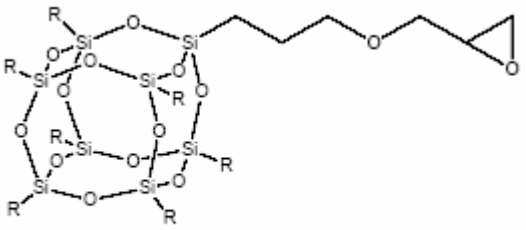
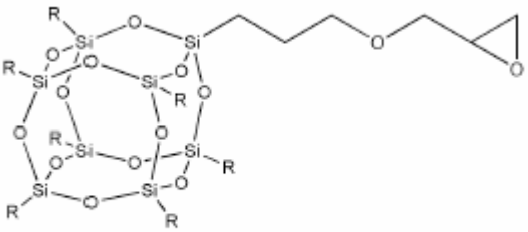
OctaAmmonium POSS $C_{24}H_{72}C_{l8}N_8O_{12}Si_8$ **Solvent Solubility**: water **Uses:** cation for surface modification	
OctaTMA POSS $C_{32}H_{96}O_{20}Si_8 \bullet \sim 60\ H_2O$ **Solvent Solubility:** water **Uses:** glassification aid TMA= trimethylamine	

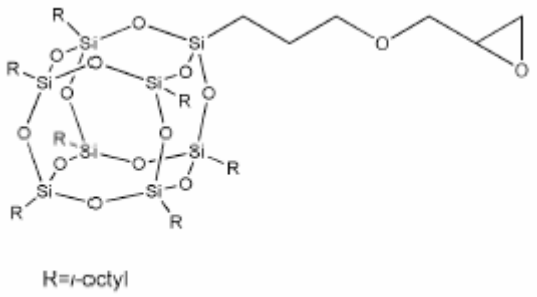
2.3.3 Epoxides

This group means that POSS units are modified with epoxide compounds. The examples of this group can be seen in Table 3.

Table 3. Modification POSS with epoxide compounds

EpoxyCyclohexylIsobutyl POSS $C_{36}H_{76}O_{13}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** impact modifier, hydrophobic epoxide, grafting agent	 R = *i*-butyl

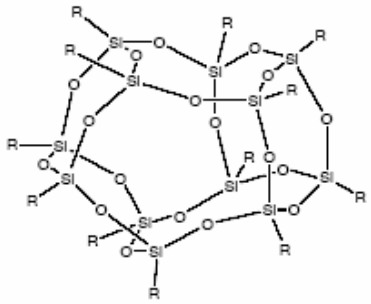
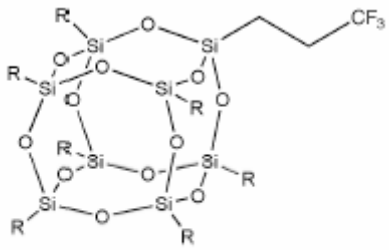
EpoxyCyclohexyl POSS $(C_8H_{13}O_2)_n(SiO_{1.5})_n$ n=8,10,12 (n=10 shown) **Solvent Solubility:** tetrahydrofuran, chloroform, isopropanol **Uses:** glassification agent, cure accelerator	
Glycidyl POSS $(C_6H_{11}O_2)$ $n(SiO_{1.5})_n$ n=8,10,12 (n=8 shown) **Solvent Solubility:** tetrahydrofuran, chloroform, toluene **Uses:** cure accelerator, toughening agent	
GlycidylEthyl POSS $C_{20}H_{46}O_{14}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** grafting agent, chain terminator	 R=ethyl
GlycidylIsobutyl POSS $C_{34}H_{74}O_{14}Si_8$ **Solvent Solubility**: tetrahydrofuran, chloroform, hexane **Uses:** grafting agent, chain terminator, improved toughness	 R=*i*-butyl

GlycidylIsooctyl POSS $C_{62}H_{130}O_{14}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** grafting agent, chain terminator, hydrophobic modification	 R=*i*-octyl

2.3.4 Fluoroalkyls

This group means that POSS units are modified with fluoroalkyl compounds. The examples of this group can be seen in Table 4.

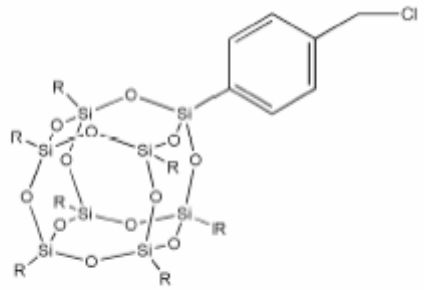
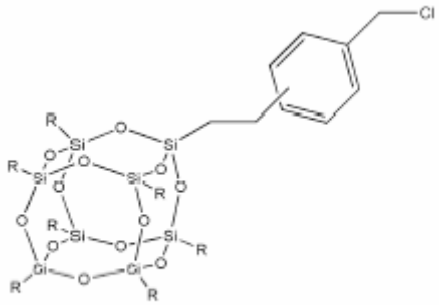
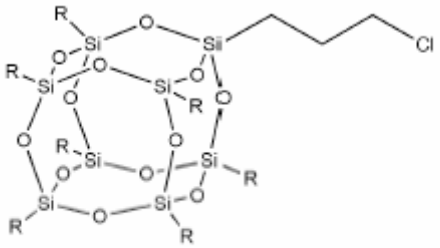
Table 4. Modification POSS with fluoroalkyls compounds

DodecaTrifluoropropyl POSS $C_{36}H_{48}F_{36}O_{18}Si_{12}$ **Solvent Solubility:** chloroform **Uses:** reduction of surface energy	 R = trifluoropropyl
TrifluoropropylIsobutyl POSS $C_{31}H_{67}F_3O_{12}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform **Uses:** reduction of surface energy and improved toughness	 R = *i*-butyl

2.3.5 Halides

This group means that POSS units are modified with halide compounds. The examples of this group can be seen in Table 5.

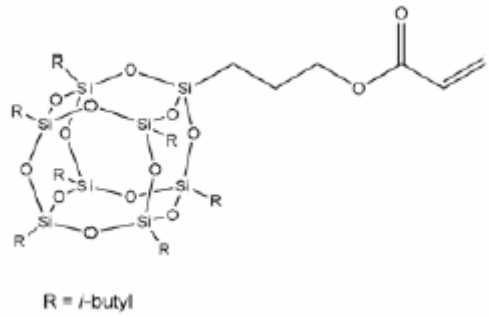
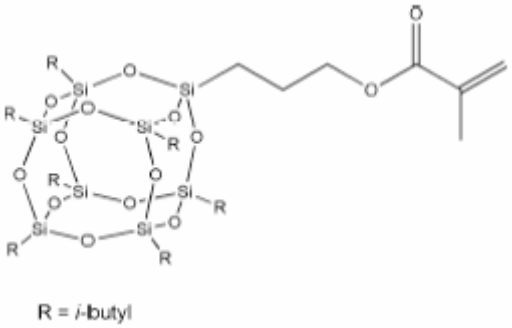
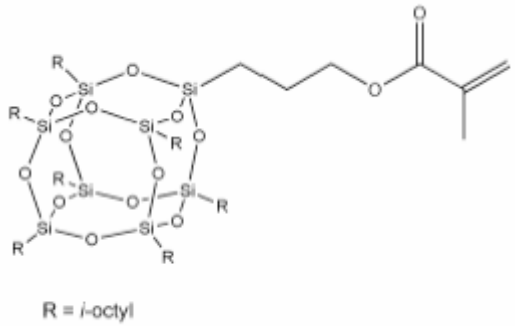
Table 5. Modification POSS with halide compounds

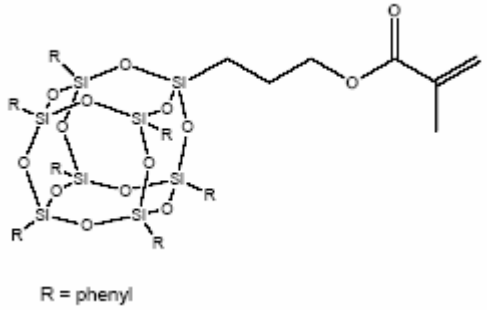
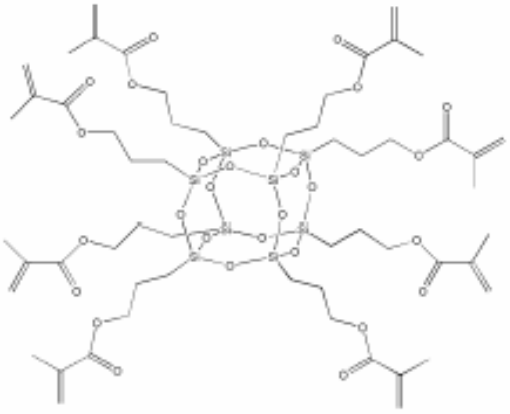
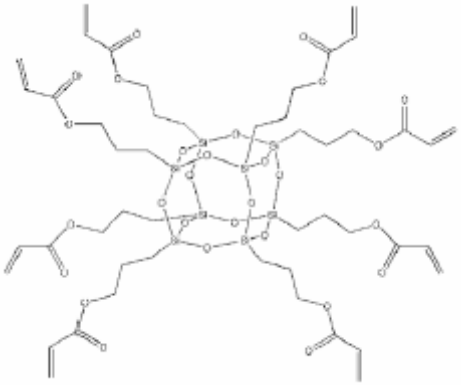
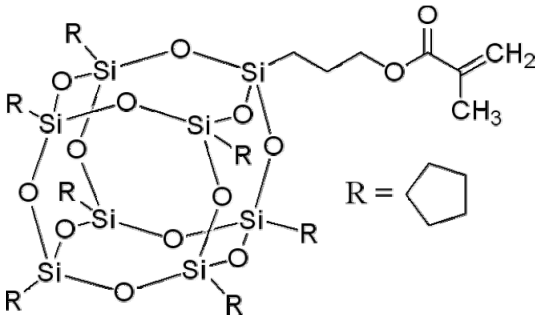
ChlorobenzylIsobutyl POSS $C_{35}H_{69}ClO_{12}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform **Uses:** graftable agent, chain terminator, improved toughness and hydrophobicity	 R = *i*-butyl
ChlorobenzylethylIsobutyl POSS $C_{37}H_{73}ClO_{12}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform **Uses:** reduction of surface energy and improved toughness and hydrophobicity	 R = *i*-butyl
ChloropropylIsobutyl POSS $C_{31}H_{69}ClO_{12}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** reagent and chain terminator, improved hydrophobicity	 R = *i*-butyl

2.3.6 Methacrylates and Acrylates

This group means that POSS units are modified with methacrylate and acrylate compounds. The examples of this group can be seen in Table 6.

Table 6. Modification POSS with methacrylate and acrylate compounds

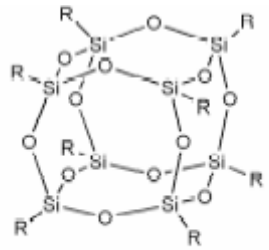
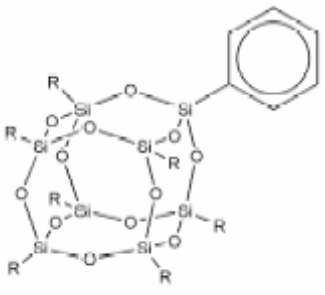
AcryloIsobutyl POSS $C_{34}H_{72}O_{14}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** comonomer for increased hydrophobicity and toughness	 R = *i*-butyl
MethacrylIsobutyl POSS $C_{35}H_{74}O_{14}Si_8$ **Solvent Solubility:** tetrahydrofuran, hexane, acetone, methyl methacrylate **Uses:** comonomer for increased hydrophobicity and toughness	 R = *i*-butyl
MethacrylIsooctyl POSS $C_{63}H_{130}O_{14}Si_8$ **Solvent Solubility:** tetrahydrofuran, hexane, acetone, methyl methacrylate **Uses:** comonomer for improved hydrophobicity and toughness	 R = *i*-octyl

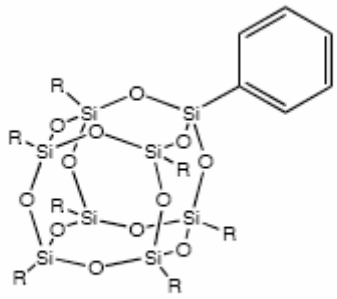
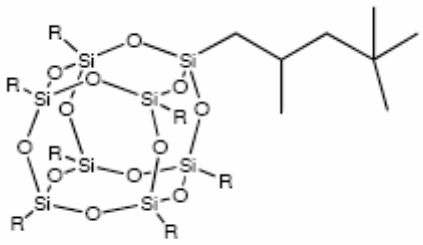
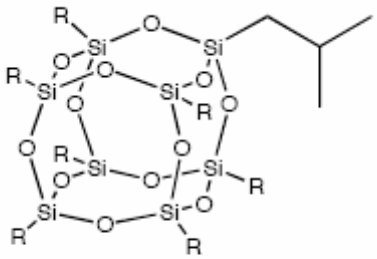
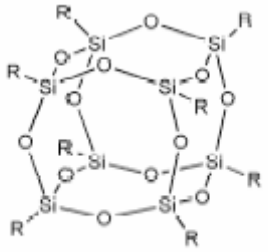
MethacrylPhenyl POSS $C_{49}H_{46}O_{14}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform **Uses:** comonomer in polymerizations	
Methacryl POSS $(C_7H_{11}O_2)_n(SiO_{1.5})_n$ n=8,10,12 (n=8 shown) **Solvent Solubility:** tetrahydrofuran, chloroform, acetone,acetonitrile, ethanol **Uses:** cure accelerator, impact modifier, porosity control	
Acrylo POSS $(C_6H_9O_2)_n(SiO_{1.5})_n$ n=8,10,12 (n=8 shown) **Solvent Solubility:** tetrahydrofuran, chloroform, acetone, acetonitrile, ethanol **Uses:** cure accelerator, impact modifier	
Propyl-POSS methacrylate $C_{41}H_{72}O_{14}Si_8$ **Uses:** as model for silica surfaces, and for the formation of novel polymeric materials.	

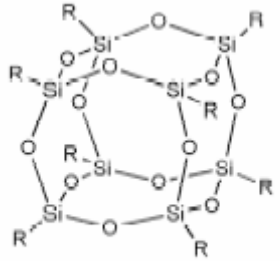
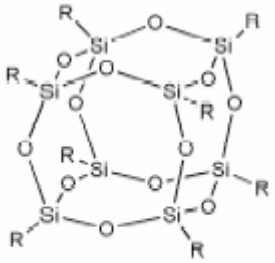
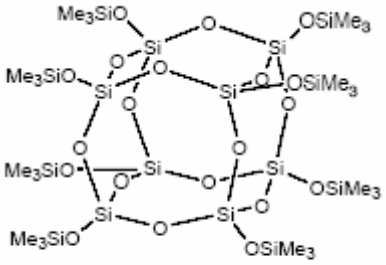
2.3.7 Molecular Silicas

This group means that POSS units are modified with aliphatic hydrocarbon. The examples of this group can be seen in Table 7.

Table 7. Modification POSS with aliphatic hydrocarbon.

DodecaPhenyl POSS $C_{72}H_{60}O_{18}Si_{12}$ **Solvent Solubility:** slightly soluble in tetrahydrofuran, toluene, chloroform **Uses:** porosity control, printability	 R=phenyl
Isooctyl POSS $(C_8H_{17})_n(SiO_{1.5})_n$ n=8,10,12 (n=8) shown **Solvent Solubility:** tetrahydrofuran, chloroform, acetone, ethanol, hexane **Uses:** hydrophobicity aid, lubricant, plasticizer	 R = *i*-octyl
PhenylIsobutyl POSS $C_{27}H_{68}O_{12}Si_8$ **Solvent Solubility:** tetrahydrofuran, cyclohexane, dichloromethane **Uses:** hydrophobicity aid for aromatic thermoplastics	 R = *i*-butyl

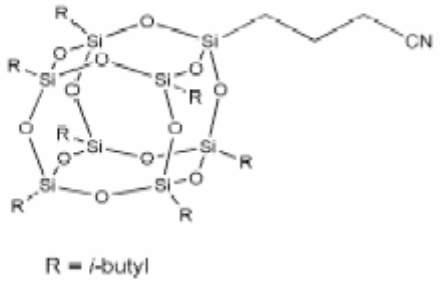
PhenylIsooctyl POSS $C_{62}H_{124}O_{12}Si_8$ **Solvent Solubility:** hexane, dichlormethan, tetrahydrofuran **Uses:** toughening agent, processing aid, hydrophobic aid	 R = *i*-octyl
IsooctylPhenyl POSS $C_{50}H_{52}O_{12}Si_8$ **Solvent Solubility:** hexane, dichlormethan, tetrahydrofuran **Uses:** toughening agent, processing aid, hydrophobic aid	 R = phenyl
IsobutylPhenyl POSS $C_{46}H_{44}O_{12}Si_8$ **Solvent Solubility:** hexane, dichlormethan, tetrahydrofuran **Uses:** toughening agent, processing aid, hydrophobic aid	 R = phenyl
OctaIsobutyl POSS $C_{32}H_{72}O_{12}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** improves hydrophobicity, printability, processing	 R = *i*-butyl

OctaMethyl POSS $C_8H_{24}O_{12}Si_8$ **Solvent Solubility**: very slightly soluble, tetrahydrofuran, chloroform **Uses:** improves hydrophobicity, printability, processing	 R = methyl
OctaPhenyl POSS $C_{48}H_{40}O_{12}Si_8$ **Solvent Solubility:** very slightly soluble, tetrahydrofuran, chloroform **Uses:** improves printability, modulus retainment	 R = phenyl
OctaTrimethylsiloxy POSS $C_{24}H_{72}O_{20}Si_{16}$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** NMR (nuclear magnetic resonance) standard	

2.3.8 Nitriles

This group means that POSS units are modified with nitrile compounds. One example of this group can be seen in Table 8.

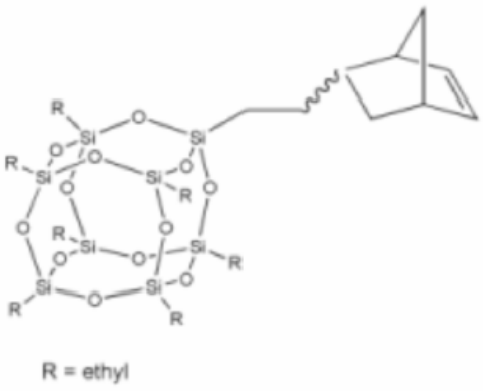
Table 8. Modification POSS with nitrile compounds

CyanopropylIsobutyl POSS $C_{32}H_{69}NO_{12}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** graftable agent, chain terminator	

2.3.9 Norbornenyls

This group means that POSS units are modified with norbornenyl compounds. One example of this group can be seen in Table 9.

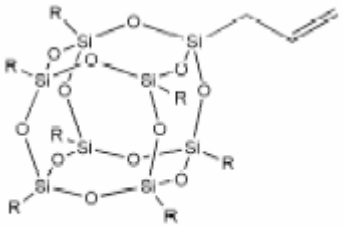
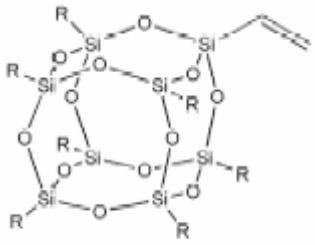
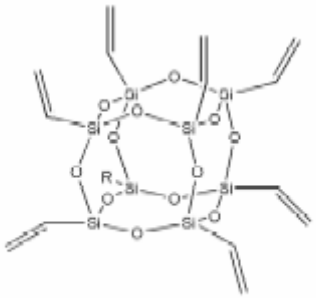
Table 9. Modification POSS with norbornenyl compounds

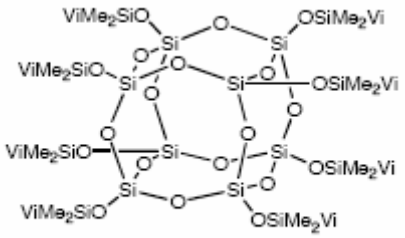
NorbornenylethylEthyl POSS $C_{23}H_{48}O_{12}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** comonomer, toughening agent, processing aid	

2.3.10 Olefins

This group means that POSS units are modified with olefin compounds. The examples of this group can be seen in Table 10.

Table 10. Modification POSS with olefin compounds

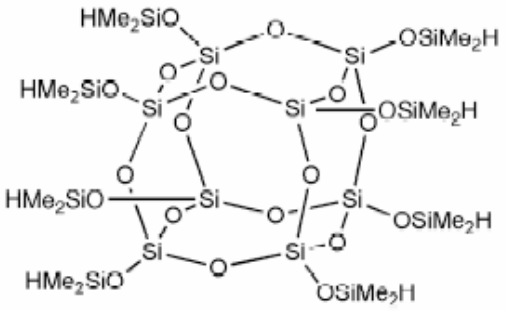
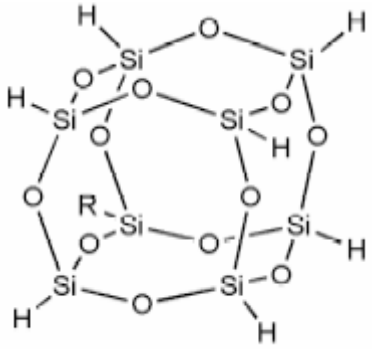
AllylIsobutyl POSS $C_{31}H_{68}O_{12}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** graftable, toughening, hydrophobic agent	 R = *i*-butyl
MonoVinylIsobutyl POSS $C_{30}H_{66}O_{12}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** graftable, toughening, hydrophobic agent	 R = *i*-butyl
OctaVinyl POSS $C_{16}H24O_{12}Si_8$ **Solvent Solubility:** methanol **Uses:** crosslinking agent	

OctaVinyldimethylsilyl POSS $C_{32}H_{72}O_{20}Si_{16}$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** crosslinker in rubber, glassification agent	

2.3.11 Silanes

This group means that POSS units are modified with silane compounds. The examples of this group can be seen in Table 11.

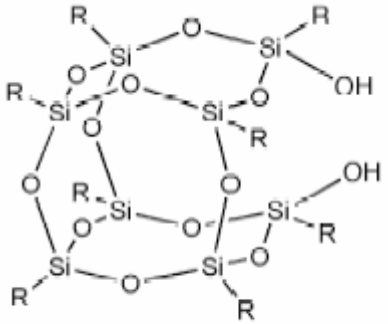
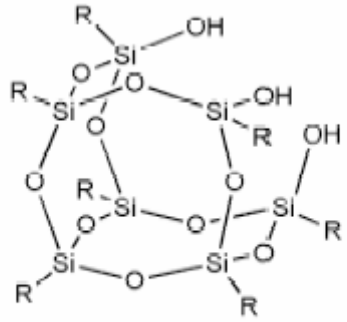
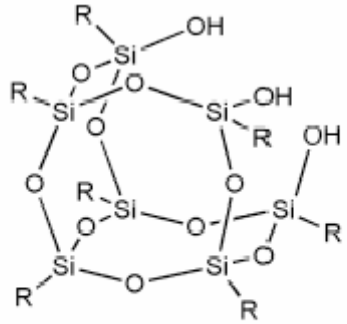
Table 11. Modification POSS with silane compounds

OctaSilane POSS $C_{16}H_{56}O_{20}Si_{16}$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** crosslinking aid, surface modification, glassification	
OctaHydro POSS $H_8O_{12}Si_8$ **Solvent Solubility:** slightly soluble in hexane and cyclohexane, chloroform, methylenechloride **Uses:** glassification agent, crosslinker	

2.3.12 Silanols

This group means that POSS units are modified with silanol compounds. The examples of this group can be seen in Table 12.

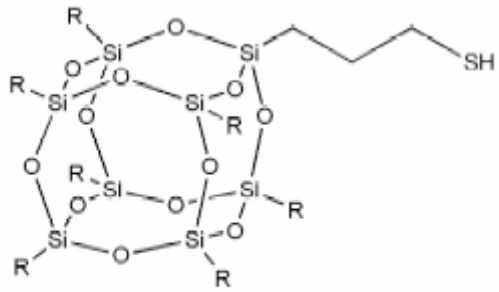
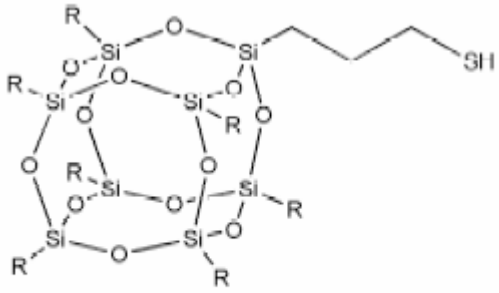
Table 12. Modification POSS with silanol compounds

DiSilanolIsobutyl POSS $C_{32}H_{74}O_{13}Si_8$ **Solvent Solubility:** tetrahydrofuran, chloroform, acetone, ethanol, hexane **Uses:** surface modification, additive to thermoplastics and thermoset polymers for improving moisture resistance and processability	 R = *i*-butyl
TriSilanolIsobutyl POSS $C_{28}H_{66}O_{12}Si_7$ **Solvent Solubility:** tetrahydrofuran, chloroform, hexane **Uses:** surface modification, additive to thermoplastics and thermoset polymers for improving moisture resistance and processability	 R = *i*-butyl
TriSilanolIsooctyl POSS $C_{56}H_{122}O_{12}Si_7$ **Solvent Solubility:** tetrahydrofuran, chloroform, acetone, ethanol, hexane **Uses:** surface modification, hydrophobicity, modulus retainment in cellulosics	 R = *i*-octyl

2.3.13 Thiols

This group means that POSS units are modified with thiol compounds. The examples of this group can be seen in Table 13.

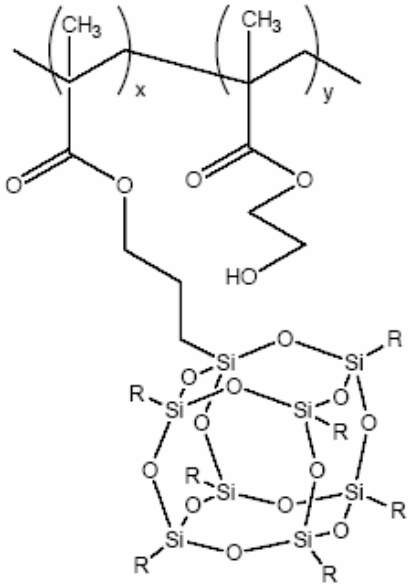
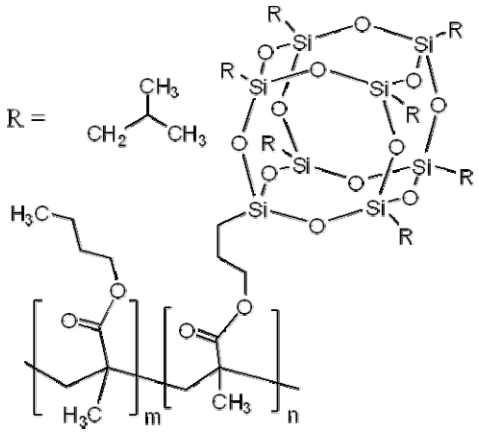
Table 13. Modification POSS with thiol compounds

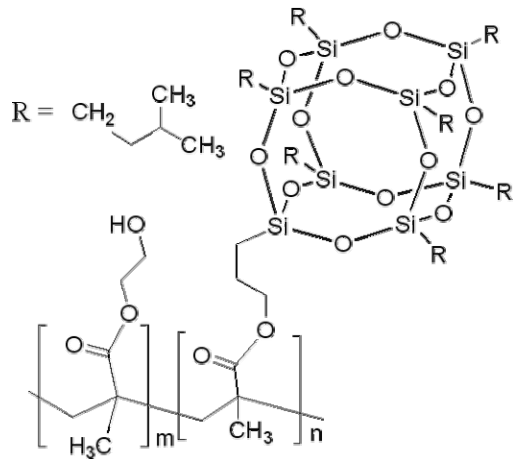
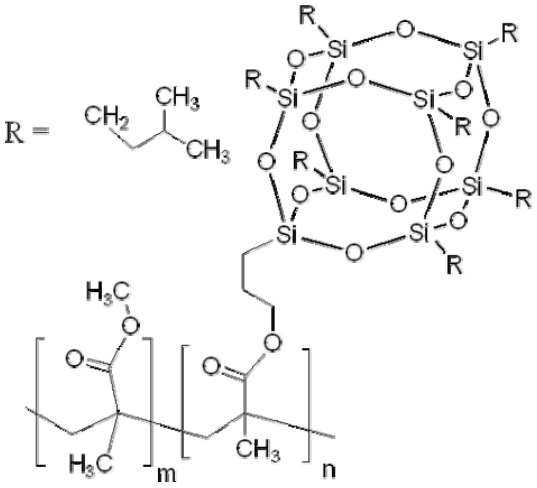
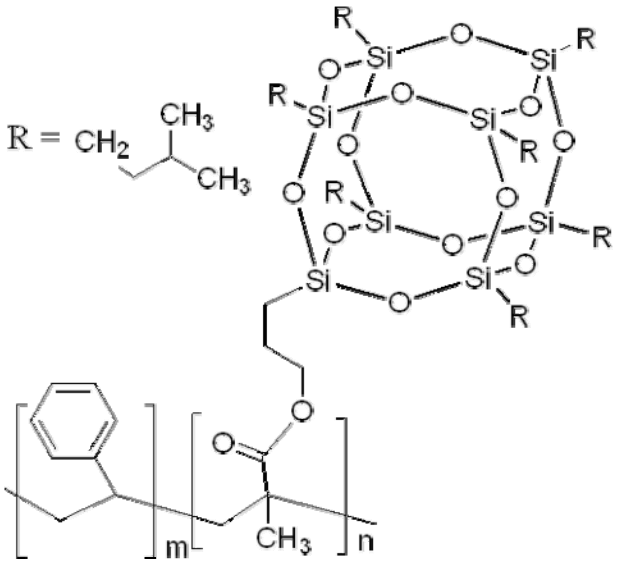
MercatopropylIsobutyl POSS $C_{31}H_{70}O_{12}SSi_8$ **Solvent Solubility:** tetrahydrofuran, chloroform **Uses:** graftable agent and surface modification, hydrophobicity improvement	 R = *i*-butyl
MercatopropylIsooctyl POSS $C_{59}H_{126}O_{12}SSi_8$ **Solvent Solubility:** tetrahydrofuran, chloroform **Uses:** graftable agent and surface modification, hydrophobicity, plasticization	 R = *i*-octyl

2.4 POSS modification with high molecular compounds

This group means that POSS units are modified with high molecular compounds, in other words polymers. The examples of this group can be seen in Table 14.

Table 14. Modification POSS with polymer compounds

Poly(methacrylpropylPOSS-co-hydroxyethylmethacrylate) **Solvent Solubility:** tetrahydrofuran, chloroform, ethyl acetate **Uses:** film former, blending agent	
Poly[(propylmethacryl-heptaisobutyl-POSS)-*co*-(*n*-butylmethacrylate)] **Solvent Solubility:** tetrahydrofuran, toluene	

Poly[(propylmethacryl-heptaisobutyl-POSS)-*co*-hydroxyethylmethacrylate] **Solvent Solubility:** tetrahydrofuran, toluene	
Poly[(propylmethacryl-heptaisobutyl-PSS)-*co*-(methylmethacrylate)] **Solvent Solubility:** tetrahydrofuran, toluene	
Poly[(propylmethacryl-heptaisobutyl-PSS)-*co*-styrene] **Solvent Solubility:** tetrahydrofuran, toluene	

2.5 POSS/polymer nanocomposites

2.5.1 POSS/PP (polypropylene) nanocomposites

Alberto Fina, Daniela Tabuani, Alberto Frache and Giovanni Camino investigated POSS in polypropylene matrixes [40]. Octamethyl-, octaisobutyl- and octaisooctyl-POSS were used as purchased from Hybrid Plastics (see Figure 21). PP was a Moplen HP501L (MFR 6.0 g/10 min at 230 °C/2.16 kg) from Basell. Composites were prepared mixing PP and POSS in a Brabender internal mixer W50E (180 °C, 10 min, 60 rpm). POSS was loaded into the polymeric matrix at different weight ratios, from 3 to 10 wt%.

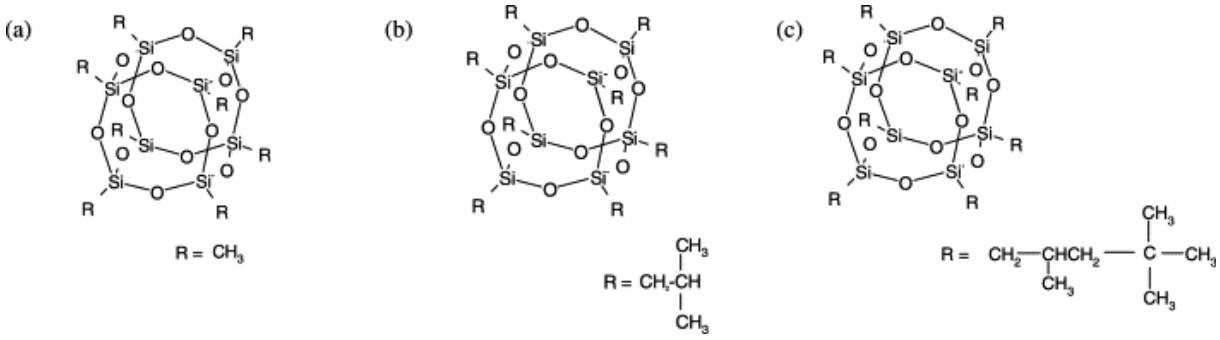


Figure 21. (a) Octamethyl-, (b) octaisobutyl-, (c) octaisooctyl-POSS cage structures.

Morphology of POSS/PP nanocomposites

Morphology of PP–octamethyl-POSS (Figure 22 a, b) shows a poor dispersion of the POSS within the polymeric matrix since micro aggregates (10–20 μm) of inorganics are found both at low and at high POSS loadings. In Figure 22 c,d are compared the fracture surfaces of neat PP and of 3 wt% octaisobutyl-POSS loaded sample: in the former no specific morphological features can be detected while the latter shows fracture lines converging in a single point indicating a spherulite morphology of the PP crystals. No POSS aggregates in the morphology of PP–octaisobutyl-POSS are visible by means of SEM analysis but TEM micrographs (Figure 22 e, f) clearly indicate the presence of POSS regular crystals with average dimensions of ca. 500 nm. POSS aggregates in morplology of PP–octaisooctyl-POSS could not be detected, neither in the 3 wt% nor in the 10 wt% composite; moreover, a spherulitic morphology could be appreciated in the 10% sample only analysing the interior of holes found within the polymeric matrix.

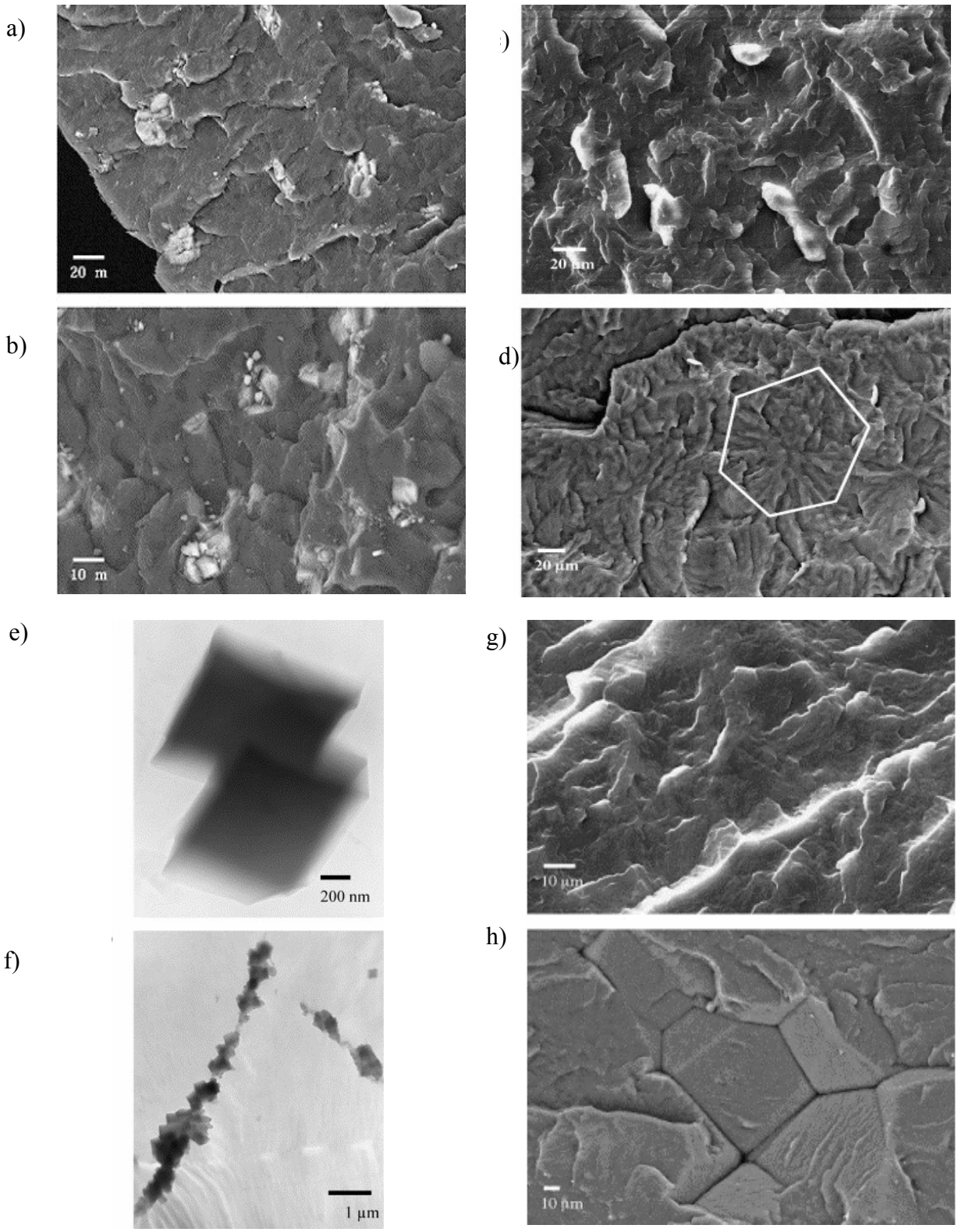


Figure 22. . ***SEM micrographs*** *of a) PP–octamethyl-POSS (3 wt%), b) PP–octamethyl-POSS (10 wt%), c) PP, d) PP-octaisobutyl-POSS (3 wt%), g) PP–octaisooctyl-POSS (3 wt%), h) PP–octaisooctyl-POSS (10 wt%),* ***TEM micrographs*** *of e) PP– octaisobutyl -POSS (3 wt%), f) PP– octaisobutyl -POSS (10 wt%).*

2.5.2 POSS/ polybenzoxazine nanocomposites

Yuan-Jyh Lee, Shiao-Wei Kuo, Chih-Feng Huang and Feng-Chih Chang investigated POSS in polybenzoxazine matrixes [41]. Octakis(dimethylsiloxy)silsesquioxane containing eight hydro-silane groups was purchased from the Hybrid Plastics Co., USA. Paraformaldehyde, phenol, and allylamine, platinum complex (Pt-dvs, 2 wt% Pt in xylene, before using the solution of the platinum complex was diluted 100-fold with xylene), toluene and the benzoxazine monomers, Pa and Ba, were used to prepare polybenzoxazine (see Figure 23 a, b). The nanocomposites with varying the amount of POSS (0, 2, and 10 wt%) were prepared

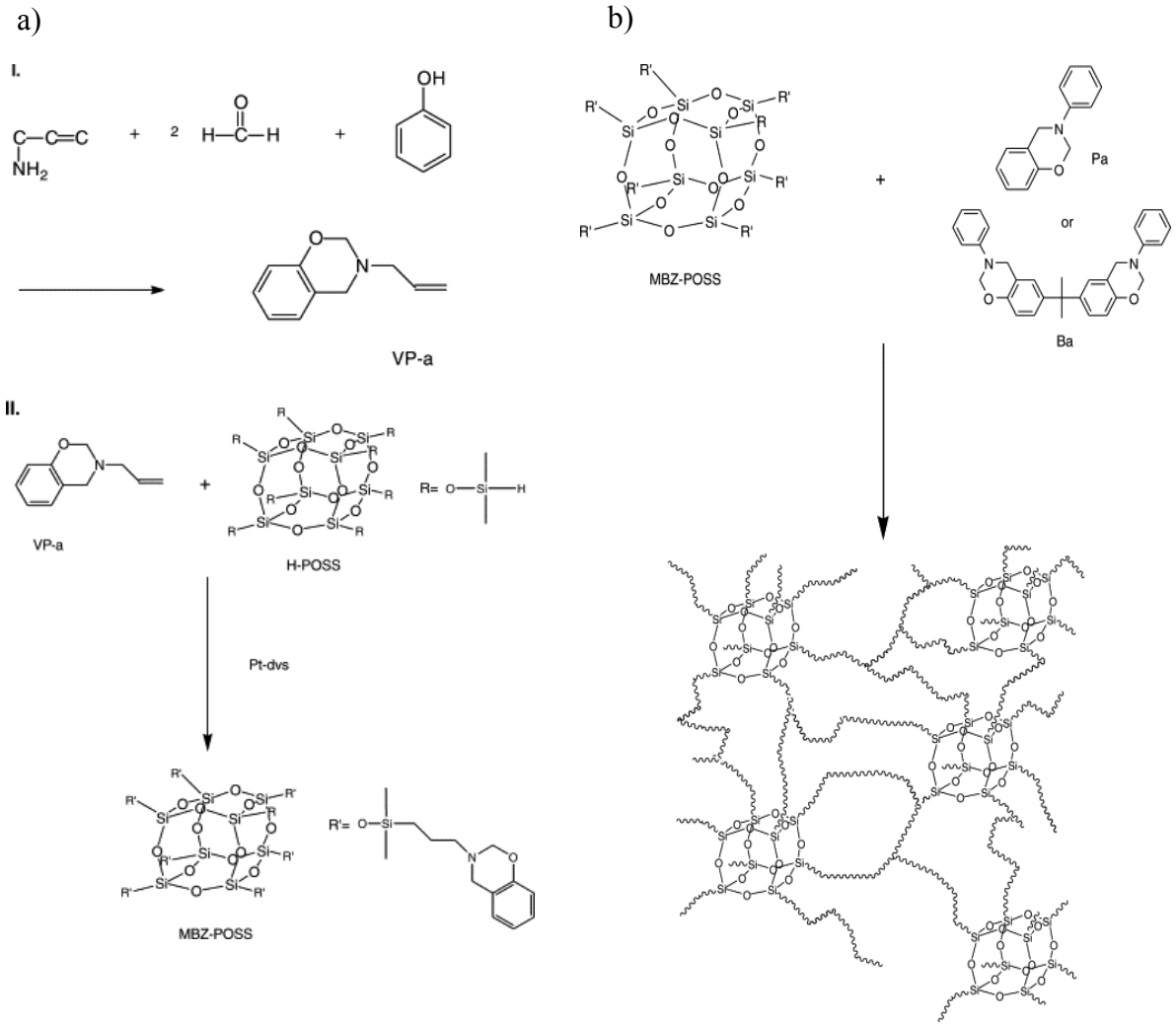


Figure 23. a) Synthesis of the VP-a and preparation of the benzoxazine-functionalized-POSS (MBZ-POSS) via a hydrosilyation, b) preparation and network structure of polybenzoxazine/POSS hybrids.

Surface analysis of polybenzoxazine/POSS composites were characterized by AFM. Figure 24. (a)–(f) displays the AFM images of hybrids having various polybenzoxazine/POSS ratios. The heterogeneous material showed the presence of different domains. Rough areas are POSS rich domains and smooth areas are polybenzoxazine rich regions. In Figure 24. (a)–(d), the degree of roughness of the Pa type polybenzoxazine/POSS hybrid films increases upon increasing the POSS content. These POSS aggregation in larger scales occur at higher POSS contents. The reason of the heterogeneous phase separation may be the less dispersive of the POSS with benzoxazine species At the same level of MBZ-POSS content (5 wt%), the POSS/Ba blend exhibits much more major aggregation than does the POSS/Pa blend. Serious aggregation of POSS occurs in the Ba type polybenzoxazine matrix because of the incompatibility of the inorganic POSS units. In the course of the formation of the polybenzoxazine/POSS network, POSS was separated from the polybenzoxazine rich region, leading to POSS rich domains in the range of 50–1000 nm.

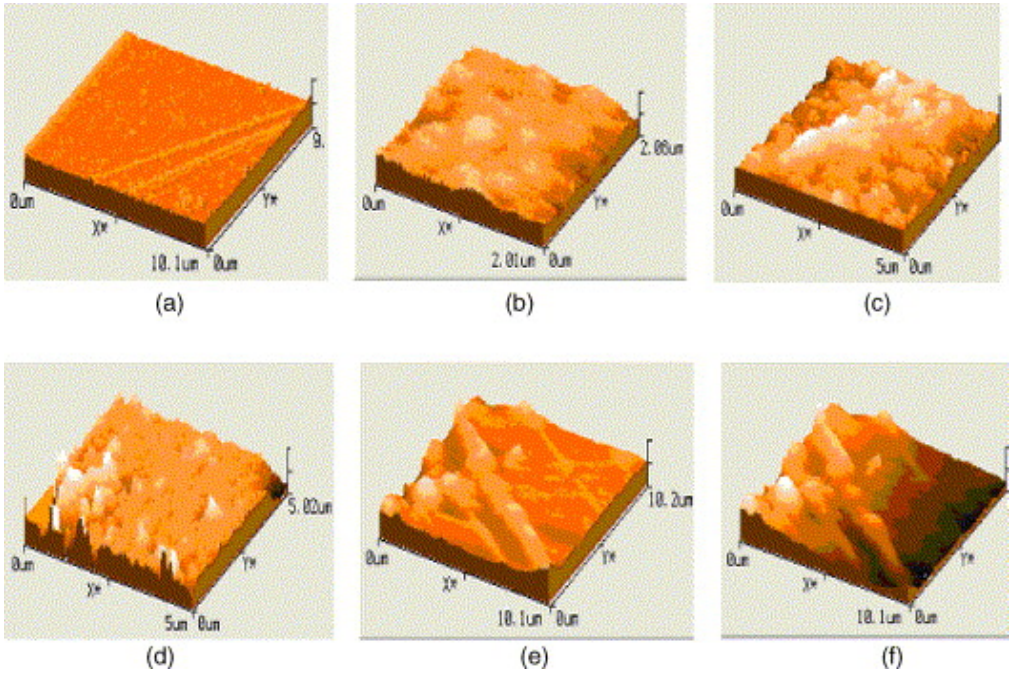


Figure 24. AFM analysis of polybenzoxazine/POSS hybrid materiale (a) pure Pa type polybenzoxazine, (b) 2 wt% MBZ-POSS content (c) 5 wt% MBZ-POSS kontent, (d) 10 wt% MBZ-POSS content (e) Ba type polybenzoxazine having 5 wt% MBZ-POSS, (f) 10 wt% MBZ-POSS content

2.6 POSS advantages and disadvantages

2.6.1 POSS advantages

POSS are attracting increased attention in nanostructured organic–inorganic hybrid materiále, because POSS self-assembly in polymer matrix will lead to interesting morphology, which is concerned with the material properties. In contrast to the clay or conventional fillers, POSS have the advantages of being monodisperse molecular weight with well-defined structure, lower density, high-temperature stability, and containing no trace metals, and sizable interfacial interaction between composite particles and polymer segments. Each POSS compound may contain one or more reactive sites; therefore, it can be easily incorporated into common polymers. It means that organic substituents attached to each cage Si atom can improve compatibility with the polymer matrix. To improve the property of the material, the POSS can be introduced into the matrix with polymerizable groups [42].

Use of POSS segments in plastics results in enhancement of the physical properties of the compositions [43]. If inorganic POSS particles are evenly distributed within the organic matrix at the nanometer scale (1–100 nm), they usually can dramatically improve the thermal stability of prepared nanocomposites. Compared to common fire retarded plastics, polymers containing POSS show delayed combustion and major reductions in heat evolution. POSS's ability to control chain motion results in usage temperature enhancement of nearly all types of thermoplastics and thermoset polymers. In many cases the glass transition can be increased by 100-200°C or even up to the decomposition temperature of the polymer. Use of POSS additives often eliminates the need to use common (dense) fillers such as silica. Depending on loading level, bulk density reductions of up to 10% have been observed with viscosity reductions of up to 24% relative to silica. POSS incorporation increases modulus and hardness while maintaining the stress and strain characteristics of the base resin. Additionally since POSS is a chemical nanotechnology, processing and moldability is maintained. Because of its chemical nature, POSS technology can be tailored to meet resin and consumer compatability needs.

Summary of POSS advantages:

- Increased Decomposition Temperature T_{dec}
- Increased Glass Transition Temperature T_g
- Reduced Flammability
- Reduced Heat Evolution
- Lower Density
- Disposal as Silica
- Extended Temperature Range
- Increased Oxygen Permeability
- Lower Thermal Conductivity
- Thermoplastic or Curable
- Enhanced Blend Miscibility
- Oxidation Resistance
- Altered Mechanicals
- Reduced Viskosity

2.6.2 POSS disadvantage

One of the disadvantages covers relatively high price of POSS nanofillers. For example concern Hybride Plastics have the prices: OctaPhenyl POSS 50grams cost 120 dollars, DisilanolIsobutyl POSS 50 grams cost 480 dollars. The next disadvantage is compatibility with polymer matrixes.

2.7 POSS application

As Additives:

- Heat/abrasion resistant paints and coatings
- Mechanical property modifiers
- Crosslinking agents
- Viscosity modifiers
- Thermal modifiers
- Fire retardants

As Plastics:

- Medical materials
- Space resistant resins
- Packaging/coatings
- Resins and elastomers
- Advanced plastics
- Composite resins
- Electronic materials
- Optical Plastics

As Preceramics:

- Ablative materials (nozzles, insulations etc.)
- Claddings/electronics coatings
- Precursors to glassy or ceramic matrices

CONCLUSIONS

A very interesting possibility to incorporate metal functionalities into polymer is to use metal containing polyhedral silsesquioxanes (POSS). POSS structure was firstly defined in 1946 by Scott [3]. Silsesquioxanes are a family of compounds with general formula $(RSiO_{1,5})_n$ where R is hydrogen or an organic group, such as alkyl, aryl or any of their derivatives. POSS structure is like a cage, where are silicon atoms with oxygene atoms bond in one complex. This unique feature allows tailoring the compatibility/reactivity with the organic polymer matrix, thus obtaining materials with specific structure and properties. POSS preperation has two steps: incompletely condensation and completely condensation. This preparation uses trifunctional monomers $RSiX_3$ (R=alkoxy, halide), which oligomerize to polyhedral oligosilsesquioxanes, randomly linked arrays of polycyclic cages.

POSS can be modified with different compounds. This bachelor thesis describes modification with metal, low molecular compounds, high molecular compounds, polymer groups.

1. POSS can be modified with metal from 1st group to 13th group of periodic table. The most usually used metal compexes containing POSS cover the following metals : Na, Ti, V, Cr, Fe, Cu.
2. POSS can be modified with low molecular compounds such as alcohols, phenols, amines, epoxides, halides, fluoroalkyls, methacrylates, acrylates, molecular silicas, nitriles, norbornenyls, olefins, silanes, silanols and thiols.
3. POSS can be modified with high molecular compounds. In most cases as a polymer bonded with POSS units are used acrylic and methacrylic derivates.
4. In recent years POSS nanofillers were used in different polymer matrixes, namely: polypropylene, polybenzoxazine, polyurethane, polycarbonate, poly(methyl methacrylate).
5. The using of POSS nanofillers in polymer matrixes can increased decomposition and glass transition temperature, oxygen permeability, reduce flammability and heat evolution, viscosity, extend temperature range, lower thermal conductivity and enhance blend miscibility. On the other hand POSS nanofillers are qiute expensive and their research is still running to reach industrial application.

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