Synthesis of Novel Ormosil Particles for Modification of Epoxy Resins

by

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"Es tan corto el amor y tan largo el olvido..."

(Love is so short, and forgetting is so long...) 

**Pablo Neruda**

*Chilean poet*

---

To my parents, Florencio and Genoveva
Abstract
Abstract

The non-hydrolytic sol-gel process has been used for the synthesis of ORganically-MOdified SILicas (ORMOSILs). The effect on morphology of the ormosil particles has been investigated using different solvents, types of stirring, and additives such as surfactants or polystyrene. Dimethyl sulfoxide has been used as a novel oxygen donor for the catalyst-free formation of colourless silsesquioxanes. The products are organic-inorganic hybrid (nano)composite materials where the organic modifications (methyl, ethyl, hexyl or phenyl groups) are covalently attached to silicon. Spherical particles of ca. 1 µm diameter were obtained in the non-hydrolytic sol-gel synthesis of methyl-modified silicate particles under certain conditions such as using Brij® 52 as surfactant and using DMSO as oxygen donor.

Product yields were generally high, and the products were characterised by Fourier transform infra-red (FT-IR) spectroscopy, $^{29}$Si nuclear magnetic resonance (NMR) spectroscopy, scanning electron microscopy (SEM) and elemental analysis (EA).

Selected ormosils were used as additives to an epoxy resin system (XLVR16-2) as toughening agents. Compatibility of the hybrid with the epoxy was varied by changing the nature of the organic group in the hybrid. The ormosil additives were uniformly dispersed throughout the resin matrix. The fracture toughness of the resin was improved using 5 parts per hundred of the resin of ethyl-modified silicate (50 % greater than that of the unmodified resin) maintaining the excellent thermal properties of the system.

Epoxy resin systems were characterised by SEM, differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and fracture toughness testing.

Emulsion polymerisation of polyhedral oligomeric silsesquioxanes (POSS) with methacrylate functionalities covalently attached to them was also investigated. Two types of polymerisation were carried out: homopolymerisation of POSS monomers, and co-polymerisation of POSS monomers with methyl methacrylate (MMA) at different molar ratios, which lead to spherical nanoparticles ranging from ca. 5 to 15 nm in diameter.
Acknowledgements
Acknowledgements

If it was difficult to write this thesis, it is probably harder to include in these few lines everybody who has helped me throughout the past few years.

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I have already expressed my thanks to my ‘family’ in England; Noelia, Ana, and Alvaro. Thanks for all the great times we have enjoyed together, including lunches, breaks and requests to bartenders to be able to watch proper sports that they do not know yet here. One day Alvaro and I will write a book about all these experiences.

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I want to dedicate this thesis to everything that I have gained coming to the UK and also to everything that I have lost leaving Spain. Everything in life has a price, and I have paid an expensive one losing the girl I thought was the one.

My parents deserve a special mention for their support over the years. Thanks to them I am doing science and I have already promised them that I will keep learning things all my life, wherever I’ll be. Finally, a big thank to my brothers, Pedro, Alvaro and Dani, for keeping me updated with such enjoyable video cassettes of Spanish handball and cycling and for being such nice guys.
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<th>Term</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>$a_0$</td>
<td>radius of a particle</td>
</tr>
<tr>
<td>AIBN</td>
<td>2,2'-azobis(isobutyronitrile)</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>ATRP</td>
<td>atom transfer radical polymerisation</td>
</tr>
<tr>
<td>$b$</td>
<td>broad infra-red absorption</td>
</tr>
<tr>
<td>BAN</td>
<td>benzoic acid anhydride</td>
</tr>
<tr>
<td>BDGB</td>
<td>1,4-butanediol diglycidyl ether</td>
</tr>
<tr>
<td>BDMA</td>
<td>benzylidimethylamine</td>
</tr>
<tr>
<td>cmc</td>
<td>critical micelle concentration</td>
</tr>
<tr>
<td>CP</td>
<td>cross-polarised</td>
</tr>
<tr>
<td>$m$-CPBA</td>
<td>meta-chloroperoxybenzoic acid</td>
</tr>
<tr>
<td>$D_c$</td>
<td>Brownian diffusion coefficient</td>
</tr>
<tr>
<td>DGEBA</td>
<td>diglycidyl ether of bisphenol-A</td>
</tr>
<tr>
<td>DME</td>
<td>dimethoxyethane, (CH$_3$O)$_2$CHCH$_3$</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>DMTA</td>
<td>dynamic mechanical thermal analysis</td>
</tr>
<tr>
<td>DP</td>
<td>direct-polarised</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>$E'(\omega)$</td>
<td>storage modulus</td>
</tr>
<tr>
<td>$E''(\omega)$</td>
<td>loss modulus</td>
</tr>
<tr>
<td>EA</td>
<td>elemental analysis</td>
</tr>
<tr>
<td>ETCS</td>
<td>ethyltrichlorosilane</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infra-red</td>
</tr>
<tr>
<td>HHPA</td>
<td>hexahydrophthalic anhydride</td>
</tr>
<tr>
<td>HLB</td>
<td>Hydrophilie-lipophile balance</td>
</tr>
<tr>
<td>HMQC</td>
<td>Heteronuclear Multiple Quantum Coherence</td>
</tr>
<tr>
<td>HTCS</td>
<td>hexyltrichlorosilane</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz</td>
</tr>
<tr>
<td>IR</td>
<td>infra-red</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>$K_{ic}$</td>
<td>critical stress intensity factor</td>
</tr>
<tr>
<td>Glossary of Terms</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>LC</td>
<td>= liquid-crystalline</td>
</tr>
<tr>
<td>LTC</td>
<td>= low temperature cure</td>
</tr>
<tr>
<td>m</td>
<td>= medium-sized infra-red absorption</td>
</tr>
<tr>
<td>MAS</td>
<td>= magic angle spinning</td>
</tr>
<tr>
<td>$M_n$</td>
<td>= number average molecular weight of polymer chain</td>
</tr>
<tr>
<td>MMA</td>
<td>= methyl methacrylate</td>
</tr>
<tr>
<td>$\eta$</td>
<td>= viscosity of a fluid</td>
</tr>
<tr>
<td>$\mu$m</td>
<td>= micrometre</td>
</tr>
<tr>
<td>mmol</td>
<td>= millimoles</td>
</tr>
<tr>
<td>MTCS</td>
<td>= methyltrichlorosilane</td>
</tr>
<tr>
<td>m.w.</td>
<td>= monomer weight</td>
</tr>
<tr>
<td>nm</td>
<td>= nanometre</td>
</tr>
<tr>
<td>NHSG</td>
<td>= non-hydrolytic sol-gel</td>
</tr>
<tr>
<td>NMA</td>
<td>= nadic methyl anhydride</td>
</tr>
<tr>
<td>NMR</td>
<td>= nuclear magnetic resonance</td>
</tr>
<tr>
<td>ORMOSIL</td>
<td>= organically modified silica or silicate</td>
</tr>
<tr>
<td>PA</td>
<td>= Phthalic anhydride</td>
</tr>
<tr>
<td>PDMS</td>
<td>= polydimethylsiloxane</td>
</tr>
<tr>
<td>PGE</td>
<td>= phenylglycidyl ether</td>
</tr>
<tr>
<td>Ph</td>
<td>= phenyl group, $-\text{C}_6\text{H}_5$</td>
</tr>
<tr>
<td>phr</td>
<td>= parts per hundred of resin</td>
</tr>
<tr>
<td>PMDA</td>
<td>= pyromellitic dianhydride</td>
</tr>
<tr>
<td>PMMA</td>
<td>= poly(methyl methacrylate)</td>
</tr>
<tr>
<td>POSS</td>
<td>= polyhedral oligomeric silsesquioxanes</td>
</tr>
<tr>
<td>ppm</td>
<td>= parts per million</td>
</tr>
<tr>
<td>PTCS</td>
<td>= phenyltrichlorosilane</td>
</tr>
<tr>
<td>$'\text{Pr}$</td>
<td>= isopropyl group, $-\text{CH(CH}_3\text{)}_2$</td>
</tr>
<tr>
<td>rev./min</td>
<td>= revolutions per minute</td>
</tr>
<tr>
<td>ROMP</td>
<td>= ring-opening metathesis polymerisation</td>
</tr>
<tr>
<td>RTM</td>
<td>= resin transfer moulding</td>
</tr>
<tr>
<td>s</td>
<td>= strong infra-red absorption</td>
</tr>
</tbody>
</table>
SBF = simulated body fluid
SDS = sodium n-dodecyl sulphate
SEM = scanning electron microscopy
sh = shoulder in infra-red absorption
sp = sharp infra-red absorption
T = absolute temperature
\( \tan \delta \) = lost tangent
TEM = transmission electron microscopy
TEOS = tetraethyl orthosilicate, \( \text{Si(OCH}_2\text{CH}_3)_4 \)
TfOH = trifluoromethanesulfonic acid
\( T_g \) = glass transition temperature
THF = tetrahydrofuran, \( \text{C}_4\text{H}_8\text{O} \)
THPA = tetrahydrophthalic anhydride
TMA = thermomechanical analysis
TMOS = tetramethyl orthosilicate, \( \text{Si(OCH}_3)_4 \)
TMS = tetramethylsilane
UV = ultraviolet
VARTM = vacuum assisted-resin transfer moulding
vs = very strong infra-red absorption
vw = very weak infra-red absorption
W = watt
w = weak infra-red absorption
\( \omega \) = angular frequency
w.t. = weight total
XPS = X-ray photoelectron spectroscopy
Chapter 1

Introduction
Chapter 1: Introduction

1.1 Aims.
The objective of this work was to investigate the applicability as polymer modifiers of different organic-inorganic hybrids to improve the mechanical toughness of a selected epoxy resin while maintaining the outstanding thermal properties.

The work programme comprised (a) the hybrid synthesis and characterisation, (b) incorporation as additives in selected polymers (epoxy resins) and (c) determination of properties of final systems.

The non-hydrolytic sol-gel route was investigated for the synthesis of ormosils. The aim was to carry out the syntheses of these hybrids under ‘pseudo dispersion polymerisation’ conditions in order to produce particles with regular shapes and low level of aggregation. Different process parameters investigated include the nature of the solvent, the stirring method and speed, and the effect of using different additives such as surfactants and polystyrene. Also different organic groups (methyl, ethyl, hexyl and phenyl) were investigated, in an effort to evaluate the effect of the organic content on the morphology of the ormosil.

The use of a solvent in the non-hydrolytic sol-gel route was expected to allow some control over the product morphology. The solvent was chosen so that the reactants were soluble at the start of the reaction, with the hybrid particles precipitating out as the reaction progresses. It was thought that the reaction might behave like a dispersion polymerisation because of the opposite polarities of the organic groups (alkyl and aryl) and the silica network, so the alkyl (aryl) groups would project into the non-polar solvent, and the more polar silica would form the core of the resulting particles. If steric stabilisation of the particles was effective, formation of spherical particles might happen.

Because the reaction is thought to work as a dispersion polymerisation, the degree of phase dispersion was expected to have a considerable effect on the morphology of the final products. Thus, different ways of stirring the mixture were investigated, such as mechanical stirrer or high speed stirrer.
Chapter 1: Introduction

The use of different additives and the effect produced on the hybrid morphology was also investigated. Surfactants are supposed to stabilise the initial dispersion of the hybrid particles, so a range of different surfactants with different polarities and their effect on the final morphology were investigated. Because the sol-gel process involves the formation of a colloidal solution, the viscosity of the reacting medium should play an important role in the final morphology of the sol-gel products. Thus, polystyrene was used to increase the viscosity and the effects on product morphology were investigated.

The ormosils obtained were characterised using infra-red (IR) spectroscopy, $^{29}$Si nuclear magnetic resonance (NMR) spectroscopy, scanning electron microscopy (SEM) and elemental analysis (EA).

The second part of the work comprised the modification of thermosetting systems such as epoxy resins using organic-inorganic hybrids as additives. The epoxy resin system investigated (XLVR16-2, Advanced Composites) is a low temperature Vacuum Assisted-Resin Transfer Molding (VARTM) resin. Resin transfer moulding may be defined as a method that uses a closed mould, pressure and vacuum (in vacuum assisted only) to transfer a low viscosity resin system into the mould. The resin system was selected to have a viscosity low enough to be used in resin injection techniques.

The resin used is a Low Temperature Cure (LTC) resin system that is cured at 60°C initially and further cured at 175°C for a short period. It is an important requirement for these systems to achieve the same toughness properties as conventional thermoplastic toughened high temperature cured materials. With that goal in mind, modification of mechanical properties (fracture toughness) while maintaining the inherent thermal properties of the unmodified resin has been explored.

The resin investigated in the present work is a trifunctional system (triglycidyl-$p$-aminophenol) and when cured with an anhydride (nadic methyl anhydride) a three-dimensional network with a high crosslink density is formed. Thus, the cured resin exhibits good high temperature performance, and hence high glass transition temperature.
Chapter 1: Introduction

However, highly crosslinked epoxy resins are known as brittle thermosetting polymers which need to be toughened for various applications. The ormosils produced are going to be used as additives to the epoxy resins as toughening agents. It is known that the improvement in the fracture toughness in silicone-modified epoxy resins increases when a decrease in the particle size of the silicone phase is produced. Therefore, low aggregation and small size of hybrid particles are targeted in the synthesis of ormosils, so a good toughening effect would be achieved.

Compatibility of the hybrid with the epoxy can be varied by changing the nature of the organic group in the hybrid; five different situations were investigated: no organic group (silica), methyl, ethyl, hexyl and phenyl substituents.

Final products were characterised in terms of morphology, thermal and mechanical properties. The fracture surface was evaluated using SEM; thermal properties were analysed with differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA); mechanical properties were investigated with fracture toughness testing.

The last part of this project involved the emulsion polymerisation of a particular type of organic-inorganic hybrid: polyhedral oligomeric silsesquioxanes (POSS) with methacrylate functionalities covalently attached to them. The parameters of the emulsion polymerisation were optimised for the synthesis of poly(methyl methacrylate) (PMMA) nanoparticles and then applied to the methacrylate-POSS reagents. Two types of polymerisation were carried out: homopolymerisation of POSS monomers, and copolymerisation of POSS monomers with methyl methacrylate (MMA) at different molar ratios.

The products obtained were characterised using IR spectroscopy, \(^1\)H NMR spectroscopy, elemental analysis, DSC, SEM and transmission electron microscopy (TEM).
Chapter 1: Introduction

1.2 Polymer dispersions.

In the present work, both sol-gel and emulsion processes involve the formation of a polymer colloid, which is a dispersion of polymer particles in a fluid. If one liquid is dispersed in another, the dispersion is called an emulsion; and if a solid is dispersed in a liquid, the dispersion is called a *sol*.

The most important methods for the synthesis of dispersions of polymer particles in a liquid medium are: dispersion polymerisation (carried out in non-aqueous, non-polar medium, where the monomer and continuous phase are soluble in each other and the polymer is not), suspension polymerisation and emulsion polymerisation (in these last two the continuous phase is water) (Table 1.1).

<table>
<thead>
<tr>
<th>Type of polymerisation</th>
<th>Typical particle radius</th>
<th>Droplet size</th>
<th>Initiator</th>
<th>Continuous phase</th>
<th>Discrete phase (particles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspension</td>
<td>&gt; 1 μm</td>
<td>~ 1-10 μm</td>
<td>Oil-soluble</td>
<td>water</td>
<td>Monomer + formed polymer in pre-existing droplets</td>
</tr>
<tr>
<td>Dispersion</td>
<td>1-10 μm</td>
<td>-</td>
<td>Oil-soluble</td>
<td>Organic (poor solvent for formed polymer)</td>
<td>Initially absent, monomer-swollen polymer particles form</td>
</tr>
<tr>
<td>Emulsion</td>
<td>50-300 nm</td>
<td>~ 1-10 μm</td>
<td>Water-soluble</td>
<td>water</td>
<td>Emulsion droplets, micelles and monomer-swollen polymer particles form</td>
</tr>
</tbody>
</table>

During the first part of the investigation, a dispersion polymerisation-like process was used for the synthesis of organic-inorganic hybrids. A typical dispersion polymerisation system is initially homogeneous; it comprises a monomer, an organic-phase initiator, an organic solvent in which the forming polymer is insoluble and a polymeric stabiliser (such as surfactant). The continuous phase is then composed of a solvent in which monomer is soluble but polymer is insoluble. When the polymer is being formed in the continuous phase, it precipitates out into a new particle phase stabilised by surfactant.
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The aggregation of growing polymer chains leads to precipitation from the continuous phase of small particles as these chains exceed a critical chain length. Coalescence of these particles with themselves and with their aggregates leads to the formation of colloidal particles which are stabilised with the surfactant covering the particle surfaces.

During the second part of the research, emulsion polymerisation was used for the polymerisation of polyhedral oligomeric silsesquioxane (POSS) reagents. Emulsion polymerisation usually leads to particles with submicron size that remain suspended in the aqueous medium, forming the so-called latex (stable colloidal dispersion of a polymeric substance in an aqueous medium). A typical emulsion system comprises water, monomer, surfactant and a water-soluble initiator. Colloidal stability is imparted by the surfactant, and when its concentration is above the critical micelle concentration (cmc) it forms micelles. At the initial stage of the emulsion polymerisation process, the monomer is present in three phases: the large monomer droplets formed by stirring and stabilised by the surfactant, the continuous water-phase which also contains the initiator, and micelles (when the concentration of surfactant is larger than the cmc). The radicals from the initiator (water soluble) are produced in the continuous phase in which polymerisation starts. Thus, the monomer is polymerised in particles (not in the droplets), which are created early in the process when initiation starts (Figure 1.1). Therefore, the droplets act only as a monomer reservoir, and provide monomer to the polymerisation loci via diffusion of the monomer molecules through the water-phase. The primary radicals formed by decomposition of the initiator in the aqueous phase add a few monomer units, forming oligoradicals, which are the origin of the final particles. Further polymerisation of the monomer leads to the formation of a new particle phase, comprising monomer and polymer, and stabilised by surfactant.
1.3 Sol-Gel processing.

The sol-gel process is a chemical synthesis method where an oxide network is formed by polymerisation reactions of chemical precursors dissolved in a liquid medium\(^4\). It was initially used for the preparation of inorganic materials such as glasses and ceramics at relatively low temperatures\(^5\). It has been in the last 20 years when this technology has been developed for the synthesis of organic-inorganic hybrids, which is nowadays one of the most interesting aspects of the process.

1.3.1 Beginning of Sol-Gel technology.

The sol-gel process was first reported 150 years ago, when in 1846 Ebelmen prepared the first metal alkoxide from SiCl\(_4\) and alcohol, observing that the product gelled on exposure to the atmosphere producing the first silica gel\(^6\). The main progress in sol-gel knowledge came in the 1930s when alkoxides were used in the preparation of oxide films to use as coatings by the Schott glass company in Germany\(^6\). However, it was not until the late 1960s and early 1970s when the ceramics industry began to show interest in gels. Roy\(^7\) developed a method where silica sols and metal carbonates, hydroxides and nitrates were combined to form gels, from which glasses were obtained by heating between 600 and
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1000°C. Multicomponent glasses were being produced using controlled hydrolysis and condensation of metal alkoxides by two different research groups\textsuperscript{8,9}.

The empirical approach of the early studies in the sol-gel process made the technological development grow faster than its own science. Only later, with the advent of modern characterisation methods, the theoretical principles began to be established; and the published work increased extraordinarily indicating the interest shown by the scientific community in this promising area\textsuperscript{4}.

1.3.2 Sol-Gel Chemistry background.

The sol-gel process offers access to a wide range of materials with very different physical and chemical properties. Although those properties make sol-gel materials interesting, the wide possibilities of material processing offered by the colloidal state make them even more attractive to science research. Also many applications of sol-gel products derive from the rheological properties of the sol and gel states which allow access to a large variety of shapes (monoliths, films, fibres, powders)\textsuperscript{4}.

The sol-gel process involves the generation of colloidal suspensions (sols) of solid particles in a liquid. During the process, these colloids are converted to viscous gels (gelation) and then to solid materials\textsuperscript{4}.

Colloidal suspensions are those in which the solid phase is so small (~1-1000 nm) that interactions are governed by short-range forces, such as van der Waals attraction and surface charges, rather than by gravitational forces.

In the sol-gel process, the most common precursors for the formation of colloidal suspensions are metal alkoxides, which consist of a metal or metalloid element (M = Si, Ti, Zr, Al, Sn, Ce...) surrounded by various alkoxide groups as ligands. Hydrolysis and condensation (in the hydrolytic sol-gel route) and direct condensation (in the non-hydrolytic sol-gel route) of metal alkoxides form large metal oxide molecules.
1.3.3 Hydrolytic sol-gel process.

Silicon alkoxides are the most popular precursors for the sol-gel process, and it is going to be described in this text as a model for the sol-gel technology. Nevertheless, many other metals like aluminium or titanium, for example, can also be used during the process. The process itself goes through different steps which are as follows:

1.3.3.1 Hydrolysis.

Silicon alkoxide are popular precursors because they react quickly with water (Equation 1.1).

\[ \text{Si(OR)}_4 + n\text{H}_2\text{O} \rightarrow \text{Si(OR)}_{4-n}(\text{OH})_n + n\text{ROH} \]  

(1.1)

The mechanism of the hydrolysis reaction (Equation 1.1) is thought to occur in 3 steps: first there is a nucleophilic attack on the silicon atom by the oxygen atom of a water molecule, then there is a transference of a proton from the water to an alkoxide group (OR) of the silicon, and finally release of an alcohol molecule (ROH)11 (Figure 1.2).

Non-silicate metal alkoxides are very reactive and generally no catalyst is needed for hydrolysis. In the case of silicon based metal alkoxides, hydrolysis (and also condensation) reactions typically proceed with either an acid or base as catalyst5. Depending on the amount and type of catalyst (acid or basic) and also on the amount of water present in the reaction medium, hydrolysis may go to completion (Equation 1.2) or stop leaving the metal alkoxide partially hydrolysed (Equation 1.1)4.

\[ \text{Si(OR)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{ROH} \]  

(1.2)
1.3.3.2 Condensation.

Depending on experimental conditions (acid or basic catalysed and concentration of the reactants), two kinds of reactions can take place: water condensation (Equation 1.3) where two partially hydrolysed molecules link together liberating a molecule of water:

\[(RO)_3SiOH + HOSi(OR)_3 \rightarrow (RO)_3Si-O-Si(OR)_3 + H_2O \quad (1.3)\]

or alcohol condensation (Equation 1.4), where a silanol molecule (partially hydrolysed silicon alkoxide) condenses with a non-hydrolysed silicon alkoxide, liberating an alcohol molecule:

\[(RO)_3SiOH + ROSi(OR)_3 \rightarrow (RO)_3Si-O-Si(OR)_3 + ROH \quad (1.4)\]

Generally, both the hydrolysis and condensation reactions occur simultaneously once the hydrolysis reaction has been initiated.

As a consequence of the use of acid or basic catalyst in both hydrolysis and condensation reactions, the structure and morphology of the resulting network strongly depends on the nature of the catalyst, in particular, the pH of the reaction. In the case of silicon alkoxides, because the hydrolysis rate is higher under acidic conditions relative to that of condensation, more linear or polymer-like molecules are going to be formed in the initial stages when using an acid catalyst. On the other hand, base catalysis results in a higher condensation rate leading to highly branched growth. Therefore, basic conditions produce dense, colloidal particulate structures because condensation reactions are directed towards the middle rather than the ends of chains.

The final structure of the sol-gel material is strongly affected by the size of the alkoxy group, which can influence the hydrolysis and condensation reaction through a steric or leaving group stability effect.

1.3.3.3 Gelation.

As the condensation reactions (Equations 1.3 and 1.4) continue, larger and larger silicon containing polymer networks are formed. Clusters grow by condensation of polymers or
aggregation of particles until the clusters collide, then links form between the clusters to produce a single giant cluster that is called a gel. The gel point is the time (or degree of reaction) at which the last bond is formed that completes this giant cluster. Therefore this gel is formed by a continuous solid skeleton that encloses a continuous liquid phase.

1.3.3.4 Ageing.
Segments of the gel network can still move close enough together to allow further condensation, which means that bond formation does not stop at the gel point. Therefore some changes in structure and properties are produced during the ageing process. During this process some gels exhibit shrinkage, which occurs because new bonds are formed where there were formerly only weak interactions between surface hydroxy and alkoxy groups. This shrinkage leads to expulsion of liquid from the pores of the gels in a process known as syneresis.

1.3.3.5 Drying.
The loss of water or alcohol from the condensation reactions takes place during the drying process via two different ways: further syneresis (expulsion of the liquid as the gel shrinks) and evaporation of liquid from within the pore structure. This process generates capillary stress, which frequently leads to cracking.

1.3.4 Non-hydrolytic sol-gel process.
1.3.4.1 Reaction.
The non-hydrolytic sol-gel (NHSG) route excludes the hydrolysis of precursors, and it is based on the direct polycondensation between a metal halide and an oxygen donor (such an alkoxide, ether or alcohol) under non-aqueous conditions. The products of the reaction are an inorganic oxide and an alkyl halide (Equation 1.5).

\[
M(OR) + m'X \rightarrow \text{product}
\]

The accepted mechanism of the NHSG process (Figure 1.3) proceeds via the coordination of the oxygen donor to the metal centre of the metal halide. The halide is then able to
attack (nucleophilic substitution) the $\alpha$-carbon in the alkoxide group and cleavage of the carbon-oxygen bond leads to an oxide linkage\textsuperscript{13-16}.

![Figure 1.3. Mechanism of the non-hydrolytic sol-gel condensation.\textsuperscript{13-16}](image)

An advantage of the non-hydrolytic route is the fact that only one stage (condensation) has to be controlled during the formation of the gel, instead of two stages (hydrolysis and condensation) in the conventional sol-gel process.

### 1.3.4.2 Precursors.

When using an alkoxide as oxygen donor, the by-product of the reaction is an alkyl halide whose nature depends on the chosen alkoxide. The alkoxy groups may be produced \textit{in situ} by the etherolysis of the metal halide if an ether is used as oxygen donor (Equation 1.6).

\[
\text{R-O-R + M-X $\rightarrow$ M-O-R + R-X} \quad (1.6)
\]

Similarly, if the oxygen donor used is an alcohol, the alcoholysis process would lead to the formation of an alkoxide (Equation 1.7).

\[
\text{R-OH + M-X $\rightarrow$ M-O-R + HX} \quad (1.7)
\]

Those two last methods (Equations 1.6 and 1.7) are particularly interesting if the alkoxide is not commercially available. The etherolysis of metal chlorides to produce some transition-metal oxides (V, Ti, Zr, Nb, W, etc)\textsuperscript{15} is an example of this pathway, which is particularly useful because the transition–metal halides are more accessible than the parent alkoxides (Figure 1.4).
As a consequence of these three different pathways for the NHSG process (Equations 1.5, 1.6 and 1.7), three different non-hydrolytic routes to oxides and mixed oxides have been proposed\textsuperscript{17}, based on the condensation between metal halides with either alkoxides, ethers or alcohols as oxygen donors.

1.3.4.3 Side reactions.

The direct polycondensation (Figure 1.3) is usually quite slow at room temperature; normally, the oxide formation needs heating between 80 and 150°C. The main reaction that takes place at room temperature in mixtures of metal halides and metal alkoxides is ligand exchange (Equation 1.8), leading to a redistribution between the alkoxide groups and the halide atoms. These rapid ligand-exchange reactions between metal alkoxides and metal halides were already described in the past\textsuperscript{18,19}.

\[ M(OR)_n + M'X_n \rightarrow M(OR)_{n-x}X_x + M'(OR)_xX_{n-x} \]  \hspace{1cm} (1.8)

An investigation to understand the ligand exchange process was carried out studying the etherolysis-condensation of titanium tetrachloride (TiCl\textsubscript{4}) with diisopropyl ether (\textsuperscript{3}Pr\textsubscript{2}O), and the direct condensation between TiCl\textsubscript{4} and titanium tetraisopropoxide (Ti(O\textsuperscript{3}Pr\textsubscript{4}))\textsuperscript{20}. In the direct condensation, the main reaction that takes place at room temperature is the redistribution of O\textsuperscript{3}Pr and Cl ligands. In the etherolysis-condensation process, the alkoxylation of TiCl\textsubscript{4} leads in a few minutes to the formation of Ti(O\textsuperscript{3}Pr)Cl\textsubscript{5}; this alkoxide starts the condensation with TiCl\textsubscript{4} before the second alkoxylation happens,
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which is much slower. Thus, the real precursors in both non-hydrolytic routes (etherolysis-condensation and direct condensation) are titanium chloro-iso-propoxide species $\text{TiCl}_4 \cdot (\text{O'}\text{Pr})_x$ in equilibrium (Equation 1.9).

\[
2\text{TiCl}_4 \cdot (\text{O'}\text{Pr})_x \rightleftharpoons \text{TiCl}_5 \cdot (\text{O'}\text{Pr})_{x-1} + \text{TiCl}_3 \cdot (\text{O'}\text{Pr})_{x+1} \quad (1.9)
\]

This example shows the complexity and the great variety of mechanisms and kinetics that may be expected for non-hydrolytic sol-gel routes to a given metal oxide.

1.3.4.4 Catalysts.

The condensation reaction results in the nucleophilic cleavage of an O-R bond and is, consequently, influenced by the electronic effects on the carbon centre from the oxygen donor. Every donor effect from the carbon group that stabilises the carbocation is going to promote the cleavage of the O-C bond$^{21}$.

When silicon is the metal centre (less reactive than other metals), this reaction works only with tertiary, benzylic and allylic carbon groups, which are able to stabilise a carbocation$^{21,22}$. If primary or secondary carbon groups are used, a Lewis acid is necessary to catalyse the condensation. Although any species with an electron-deficient atom can act as a Lewis acid (the simplest example is $\text{H}^+$), the most common Lewis acids are anhydrous metal salts, such as iron or aluminium chloride. In the literature, an excellent study of the use of such catalysts for the preparation of silica by condensation of silicon tetrachloride with different oxygen donors was reported by Corriu and co-workers$^{16}$. They studied the efficiency of metal chlorides in the catalysis of the condensation of $\text{SiCl}_4$ with $\text{Pr}_2\text{O}$, concluding that the most effective catalyst for this type of condensation was iron(III) chloride ($\text{FeCl}_3$). The efficiency of the anhydrous metal salts decreased in the order: $\text{FeCl}_3 \gg \text{AlCl}_3 \sim \text{ZrCl}_4 > \text{TiCl}_4$ $^{16}$.

The mechanism of the catalysed condensation of a silicon chloride with an alkoxide (Figure 1.5) starts with the reversible coordination of the oxygen of the metal alkoxide to the silicon centre of the silicon chloride. The formation of a coordinate complex with the catalytic species leads to nucleophilic attack of the chloride ion on the $\alpha$-carbon in the
alkoxy group, and the pair of electrons from the old O-Et bond then form an oxobridge between the metal and the silicon atom (M-O-Si)\(^{16}\).

![Figure 1.5. Mechanism of condensation of a silicon chloride with a metal alkoxide using FeCl₃ as catalyst\(^{16}\).](image)

1.3.5 Non-hydrolytic sol-gel route for metal oxides.

The non-hydrolytic sol-gel method permits the formation of metal oxides in one step without the use of any complexing agents or other additives. This approach is based on a procedure of preparing non-metal oxides reported by Gerrard \textit{et al.}\(^{23}\), but it was first reported with metal components by Corriu \textit{et al.}\(^{24}\). Depending on the nature of the precursors, many different inorganic oxides can be obtained; silicon oxide, aluminium oxide and titanium oxide are going to be reviewed.

1.3.5.1 Silicon oxide.

The reaction of different silicon tetrahalides with various organic oxygen donors such as \textit{tert}-butanol, allyl alcohol, benzyl alcohol, benzaldehyde and dibenzylether was investigated by Corriu \textit{et al.}\(^{21}\). They found silicon tetrabromide more reactive than silicon tetrachloride because of the higher polarisability of bromine, which makes it a better leaving group.

Although the NHSG route has been successfully used for the preparation of different metal oxides, in the case of silica, the silicon chloride-silicon alkoxide (Si-Cl/Si-OR)
condensation without using a catalyst works only with tertiary, allylic and benzylic R groups, which are able to stabilise the carbocation\textsuperscript{21}. Gerrard and Kilburn\textsuperscript{25} reported that alcohols containing a phenyl group far from the 1-carbon atom of the alcohol only formed the silicon tetraalkoxide; whereas those with a phenyl group attached to the 1-carbon atom (benzylic alcohol) gave alkyl chloride and silica (Figure 1.6).

\[
\text{SiCl}_4 \rightarrow \text{Si}^{+} + 4\text{HCl} \quad \text{(Figure 1.6. Different reactivity of alcohols towards silicon tetrachloride\textsuperscript{25}.)}
\]

Tertiary alcohols such as tert-butyl alcohol and 2-methylbutan-2-ol reacted in a similar way to 1-phenylethanol, except that the reaction was slow at room temperature\textsuperscript{26}. When the mixture was warmed, the reaction became vigorous and silica was rapidly formed. As a by-product the corresponding alkyl chloride was obtained.

The low reactivity of silicon tetrachloride towards some primary and secondary oxygen donors such as diethyl ether or diisopropylether was overcome with the use of Lewis acids as catalysts\textsuperscript{16}.

The unreactivity of silicon tetrachloride towards tetraethoxysilane (TEOS) reported by Bourget \textit{et al.}\textsuperscript{21} was solved with the use of a catalyst (Equation 1.10). In the presence of FeCl\textsubscript{3} as catalyst, silica oxides were obtained by reacting silicon tetrachloride with tetraisopropoxysilane, tetraethoxysilane, diisopropyl ether, or diethyl ether as oxygen donors\textsuperscript{14}.

\[
\text{SiCl}_4 + \text{Si(OC}_{\text{Et}}\text{)}_4 \xrightarrow{\text{FeCl}_3} 2\text{SiO}_2 + 4\text{EtCl} \quad \text{(1.10)}
\]
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The effect of the amount of catalyst and the reaction temperature on the condensation of silicon tetrachloride with TEOS (Equation 1.10) was investigated\(^{28}\), and it was concluded that an iron(III) chloride level of 0.8% by weight at 90°C reaction temperature showed the best balance between fast reaction and enough time to homogenise the reacting species.

1.3.5.2 Aluminium oxide.

Aluminium oxide has been prepared by the condensation of aluminium halides \( \text{AlX}_3 \) (\( X = \text{Br, Cl} \)) with aluminium alkoxides \( \text{Al(OR)}_3 \) such as isopropoxide and secbutoxide\(^{29,30}\) (Equation 1.11) and other oxygen donors such as diisopropylether at around 100°C.

\[
\text{AlX}_3 + \text{Al(OR)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{RX}
\]

(Equation 1.11)

During the reaction of aluminium chloride (solubilised by formation of an addition complex with ether) with aluminium triisopropoxide, a high proportion of pentacoordinate aluminium atoms were observed by \(^{27}\text{Al} \) NMR spectroscopy\(^{31}\). Normally, aluminium oxide contains tetracoordinate or hexacoordinate Al atoms, and pentacoordinate atoms have been found in only a very few examples\(^{14}\). The pentacoordinate form is thought to happen because aluminium chloride and aluminium triisopropoxide form a trinuclear aluminium complex (Equation 1.12) in which one aluminium atom is pentacoordinate and the other two are tetracoordinate\(^{14}\) (Figure 1.7). These five-coordinate Al sites are quite unusual in aluminas and might be of interest in the area of catalysis.

\[
2\text{AlCl}_3 + 2\text{Al(O}^\text{Pr})_3 \rightarrow \text{AlCl(O}^\text{Pr})_2 + \text{Al}_3\text{Cl}_5(O^\text{Pr})_4
\]

(Equation 1.12)

\[\text{Figure 1.7. Structure of the trinuclear complex obtained from AlCl}_3 \text{ and Al(O}^\text{Pr})_3.\]

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The effects of different oxygen donors towards the condensation of aluminium trichloride, such as benzaldehyde (Equation 1.13), tetrahydrofuran (THF) and diethylether were investigated. The last two needed the presence of 1% of iron(III) chloride as catalyst. The reaction was completed in a shorter time than using silicon tetrachloride under the same conditions, reflecting the higher reactivity of aluminium compared to silicon.

\[ 2\text{AlCl}_3 + 3\text{PhCHO} \rightarrow \text{Al}_2\text{O}_3 + 3\text{PhCHCl}_2 \] \hspace{1cm} (1.13)

1.3.5.3 Titanium oxide.

Using the non-hydrolytic sol-gel method to prepare TiO\(_2\), different crystalline structures were obtained after calcination depending on the nature of the oxygen donor. Titanium dioxide is known to exist in three crystalline modifications: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). The reaction of diethyl ether with TiCl\(_4\) at 110\(^\circ\)C produces anatase (which starts to convert into rutile only around 1000\(^\circ\)C). Reaction of TiCl\(_4\) with ethanol yields rutile at relatively low temperature (110\(^\circ\)C). Finally, brookite (which is very uncommon in synthetic routes) was produced reacting tert-butyl alcohol with titanium chloride at 110\(^\circ\)C. This study shows the ability to control the crystalline structure of a metal oxide depending on the nature of the oxygen donor (as the conventional sol-gel methods do by controlling the hydrolysis conditions).

TiO\(_2\) nanocrystals have been obtained when reacting titanium alkoxides with titanium halides at high temperature (300\(^\circ\)C). The classical method for the synthesis of titania\( ^{15,20} \) was employed with only a difference in using higher temperature (Equation 1.14). Nanocrystalline products are obtained at elevated temperatures because TiX\(_4\) works as a crystallization agent as well as reactant in the condensation (Equation 1.14). Apart from the normal condensation process, the halide may attack the electrophilic titanium centre of the alkoxide precursor or of a partially formed titania network. This results in halide/alkoxide or halide/titanyl exchange, which leads to Ti-O bond breaking and forming (a reversible chemical process that erases defects incorporated into a growing titania crystal).
\[
\text{TiX}_4 + \text{Ti(OR)}_4 \rightarrow 2\text{TiO}_2 + 4\text{RX} \quad (1.14)
\]

In the early exploration of the mechanism of the NHSG condensation, titania synthesis was investigated using titanium tetrachloride with a number of different oxygen donors\textsuperscript{13,15,20,28}. Reacting titanium tetrachloride with titanium tetraisopropoxide (see section 1.3.4.3) and with different ethers such as THF, di(n-propyl)ether, diisopropyl ether and dimethoxyethane (DME), the role of the oxygen donor was investigated. Gelation took longer in all cases than under hydrolytic conditions. It was found that the gel time was dependent on the oxygen donor and increased in the order: Ti(O'Pr)$_4 \sim$ 'Pr$_2$O $< \text{Et}_2$O $<$ THF $< n\text{Pr}_2$O $<$ DME\textsuperscript{13}.

Benzaldehyde was added to TiCl$_4$ as oxygen donor (it reacts with SiCl$_4$ in presence of a catalyst and with AlCl$_3$ without any catalyst species) but the premature solidification of the intermediates (Equation 1.15) impeded the reaction to proceed further and titanium oxide was not obtained\textsuperscript{28}.

\[
\text{TiCl}_4 + \text{R-O-R} \rightarrow \text{Cl}_3\text{Ti-OR} + \text{R-Cl} \quad (1.15)
\]

1.3.5.4 Binary oxides.

Different metals can be used to form binary mixed metal oxides via a cross-condensation reaction (Equation 1.5). The control of the composition and homogeneity in binary oxides is difficult to achieve using the conventional hydrolytic sol-gel process, because of the different reactivities of alkoxide precursors towards hydrolysis and condensation. Homogeneity is based on the rate of homocondensation (which is the formation of structures such as M-O-M and M'-O-M') compared to the rate of heterocondensation (formation of M-O-M' bridges). It is accepted that non-hydrolytic routes lead to better control over the molecular level homogeneity and composition than hydrolytic routes\textsuperscript{17}. This is thought to be because of the levelling of the heterocondensation and homocondensation rates, which is a consequence of the mechanism of the reaction (Figure 1.3), which allows the formation of a high level of mixed M-O-M' bridges.
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Many binary metal oxides have been investigated using the NHSG, including silicon-titanium\textsuperscript{17,24,34,35}, silicon-aluminium\textsuperscript{24,34}, titanium-aluminium\textsuperscript{24,34,36,37}, silicon-zirconium\textsuperscript{24,35,38}, aluminium-zirconium\textsuperscript{39}, titanium-zirconium\textsuperscript{40,41}.

1.3.6 Limitations of sol-gel processing.

Even though sol-gel technology has been found very useful in so many different areas of materials processing, some limitations have been found\textsuperscript{10}. The precursors are sometimes expensive and moisture sensitive, leading to problems in large scale production plants. The process is also quite long, specially when ageing and drying have to be done with special care. Shrinkage and stress cracking during drying are phenomena that require careful attention during processing.

Sometimes, steric factors have a strong influence on the course of the reaction, impeding the condensation reaction from proceeding to completion. In the present work, the condensation of alkylchlorosilanes with alkoxysilanes was investigated. The reaction was observed not to proceed to completion, leading to the presence of residual groups such as (RO)\textsubscript{2}Si(OSi)\textsubscript{2}, (RO)\textsubscript{3}Si(OSi)\textsubscript{2} or (RO)\textsubscript{3}Si(OSi).

1.4 Organic-Inorganic Hybrids.

The synthesis of organic-inorganic hybrid materials has received much attention in the past several years because of the possibility of developing materials with unique structures and properties. There has been an increase in the number of publications dedicated to this topic, including some interesting reviews\textsuperscript{5,11,42,43,46,47,56,57}, indicating the growing interest of chemists, physicists and materials researchers in this new area.

In these hybrid materials the most important properties of their constituents are combined, like, for example, high transparency (glass-like) and relatively low processing temperatures (polymer-like).

The synthesis, characterisation, and applications of organic-inorganic materials have become such an expanding area of interest in materials science that many researchers are
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speculating that if the 19th century was the century of ceramics and the 20th century belonged to polymers, the 21st century will be the age of hybrids. Some of the earliest organic-inorganic hybrids are derived from the paint and polymer industries, where to improve optical and mechanical properties, inorganic pigments or fillers were dispersed in organic components (solvents, surfactants, polymers, etc).

1.4.1 Classification of hybrids.

There are two kinds of classification of these hybrid materials: one by Novak that has been used during the past, and another one by Sanchez, which has been accepted nowadays as the best classification method.

Novak divided these hybrid materials into five major types based on their macromolecular structures and phase connectivities:

Type I: Soluble, preformed organic polymers embedded in an inorganic network. The fastest way of producing this class of hybrids is through the sol-gel process, which involves the inorganic hydrolysis and condensation reactions in the presence of a preformed organic polymer.

Type II: Embedded, preformed organic polymers covalently attached to the inorganic network. The main difference with type I hybrids is the introduction of covalent bonds between the inorganic and organic phases. These kind of materials are normally prepared through a standard sol-gel process with the polymers possessing trialkoxysilyl moieties, \(-\text{CH}_2\text{Si(OR)}_3\). The organic content of the polymer remains unreacted, while the pendant silyl group is readily incorporated into the inorganic structure.

Type III: Mutually interpenetrating organic-inorganic networks. Selecting the right conditions, the organic polymer can be kinetically trapped within the organic matrix before phase separation takes place. An advantage of this method is that transparent
organic-inorganic hybrids can be formed which contain organic polymers that would normally be insoluble in typical sol-gel conditions.

*Type IV:* Mutually interpenetrating networks with covalent bonds between the organic and inorganic phases\textsuperscript{46}. Following the procedure of introducing covalent bonds between the two phases observed in type I and II hybrids, the same pathway can be introduced to convert type III materials into type IV, by incorporating covalent bonds between the organic and inorganic phases.

*Type V:* “Non-shrinkage” sol-gel materials\textsuperscript{46}. During the synthesis of the previous types of hybrids, shrinkage of the gel was found to be a problem. In this kind of hybrids, this problem was overcome by substituting the usual alkoxide groups on the precursors with polymerisable alkoxide groups, so the alcohol liberated during the process is polymerised, and evaporation of the by-products is not needed. Thus large scale shrinkages are avoided.

Clément Sanchez has published the most widely accepted classification of hybrids\textsuperscript{11}, depending on the nature of the interface or of the links and interactions exchanged by organic and inorganic components. This more recent classification falls into two different categories:

*Class I:* In this kind of material organic and inorganic components are linked together through weak interactions such as van der Waals, ionic or hydrogen bonding and electrostatic forces\textsuperscript{11}.

*Class II:* These materials are hybrid structures in which organic and inorganic contents are grafted together through strong covalent or ionic-covalent chemical bonds\textsuperscript{11}.

### 1.5 Sol-Gel hybrids.

Combining inorganic components with organic moieties on a microscopic or nanoscopic scale needs a formation process of the inorganic network which is compatible with the
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thermal stability of the organic components. Organic materials can rarely survive temperatures higher than 200°C, but classical inorganic methods commonly work around 1000°C. The sol-gel process overcomes this limitation and permits low temperature routes to organic-inorganic hybrids.

The sol-gel process has been found to be the best method for the synthesis of organic-inorganic hybrids because its practical advantages include low temperature reaction; the ability to control the final composition (the choice of the reaction conditions leads to the control of the material structure and properties); and convenience for the formation of various shapes.

The synthesis of organic-inorganic hybrids via the conventional sol-gel process (hydrolytic route) has been intensively explored over the last 20 years or so. However, not much research has been carried out in the field of hybrids via the non-hydrolytic sol-gel route, and the different kinetic and electronic factors during the process offer an alternative route to some hybrids whose synthesis using the hydrolytic route may have problems such as incompatibility of the precursors with water.

1.6 Organically Modified Silicas (Ormosils).

The chemistry of organic-inorganic hybrids has been mainly developed around silicon-containing materials because the chemistry of silicon alkoxides is very well known and the reactivity of silicon alkoxides is low and easy to control. Those hybrids with organic groups attached to silicon are often abbreviated as Ormosils (ORganically MODified SILicas or silicates). They are defined as silicate networks (inorganic component of the hybrid) that are organically modified by the covalent attachment of small organic groups to some or all the silicon atoms in the network.

In the synthesis of ormosils, the inorganic precursors either already have a chemically attached organic moiety, e.g., alkylchlorosilanes, or chemical bonds are formed when reactions occur between the two components in the liquid solution in the hybrid gel (that is the case of polydimethylsiloxane (PDMS) and TEOS).
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1.6.1 Historical background of Ormosils.

The Organically Modified Silicas were first reported in a major way in the literature in the mid 1980s by two different research groups: Schmidt group\(^{57-60}\) (who were developing a hard contact-lens material) and Wilkes group\(^61\) (who were trying to modify some properties of sol-gel glasses). However, the first report about a silica network modified by small organic groups was back in 1957. Andrianov and co-workers\(^{62}\) synthesised a range of alkyl- and aryl- modified silicates and linear polyorganosiloxanes. They investigated the condensation of some organochlorosilanes such as methylphenyldichlorosilane, dimethyldichlorosilane and phenyltrichlorosilane with phenyltrithoxysilane and ethylphenyldiethoxysilane. The reaction was observed to work more efficiently when using a catalyst such as iron(III) chloride (preferred catalyst) or aluminium(III) chloride. The obtained products were linear and branched polyorganosiloxanes and ethyl chloride as by-product.

These new inorganic-organic hybrids were named “Ormosils” by Schmidt and “Ceramers” by Wilkes. Schmidt found out that the best way to introduce an organic group into an inorganic network was the use of organo-substituted silicon esters in a polycondensation process\(^60\). By the use of the sol-gel process they developed different groups of materials with common properties: scratch resistance (based on epoxysilane with inorganic network formers; epoxy ormosils were developed as contact lens materials), thermoplastics (based on different contents of phenylsilane, with the potential use as coatings, adhesive films and bulk materials), photocurable materials (based on photocurable ligands like methacrylate, vinyl or allyl groups) and porous materials (formed using a high content of inorganic network formers and mainly monofunctional organosilanes).

On the other hand, in 1985 Wilkes initiated the development of novel organic-inorganic hybrid materials by reacting metal alkoxides with functionalised polymeric/oligomeric species\(^61\). The system of PDMS and TEOS was the first one successfully prepared. PDMS oligomers with low molecular weight terminally functionalised with silanol groups were introduced into a network with TEOS using an acid catalyst.
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Since the pioneering research of Schmidt and Wilkes, hundreds of publications on ormosils have appeared. Two possible reasons can be presumed for all this research interest\textsuperscript{56}. The synthesis of such new materials and the understanding of the reactions in solution and structures of the hybrids can be enough justification for the research. The other reason is that these materials are expected to have unique and useful properties, because of the combination of both organic and inorganic phases.

The big impact of these materials within the scientific community is due to the possibility of combining organic and inorganic materials, with the direct repercussion on the properties and possible applications of these materials. All these published studies validate the prediction made by Dr. Rochow, the “grand old man” of silicones, expressed during a talk given by him in the early sixties in Munich. “There must be a way to combine inorganic and organic materials into a new type of products, using the basic principles of silicone preparation” (which is almost identical with the sol-gel process), “and this task should be solved by the following generation of researchers”\textsuperscript{59}.

1.6.2 Types of Ormosils.

Those Ormosils with precursors such $\text{RSi(OR')}_3$, where R is an organic terminal group which does not form a bridge in the gel network (Figure 1.8), are the simplest\textsuperscript{56}. These precursors are very popular because a variety of such silanes are commercially available. Bifunctional alkoxy silanes such $\text{R}_2\text{Si(OR')}_2$ have to be used in the presence of higher functionality precursors in order to form a three-dimensional network. Because the organic groups have been chemically bonded with the inorganic component before the reaction starts, a careful selection of the structure of the organic group would allow control of some properties of the resulting material, such as mechanical, optical or electrical properties\textsuperscript{5}.

\[ \text{R} - \text{Si-O-Si-O-} \]

\[ \text{O} \quad \text{O} \]

\[ \text{R} \quad \text{O} \quad \text{R} \]

\textbf{Figure 1.8}. Network formed with the simplest class of Ormosils\textsuperscript{56}. 24
Another new family of these hybrids is the polyhedral oligomeric silsesquioxanes (POSS materials). They are formed from the monomeric precursor shown in Figure 1.9, where R is a non-reactive group and Y can be polymerised\textsuperscript{56}.

![Figure 1.9. Structure of the precursor monomer of POSS materials\textsuperscript{56}.](image)

This monomer has been mixed with different organic polymers such as poly(methyl methacrylate) (PMMA) to produce a large number of new materials. It is possible to think that these cubic silsesquioxanes could be the smallest silica particles possible. A literature review on these materials can be found in Chapter 4 of this thesis.

One particular group of polysilsesquioxanes is bridged polysilsesquioxanes (Figure 1.10) and they are formed from monomers that contain a variable organic bridging group and two or more trifunctional silyl groups\textsuperscript{52,63-66}.

![Figure 1.10. Bridged polysilsesquioxane\textsuperscript{52}.](image)
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This type of ormosils can be prepared with a large variety of different organic bridging groups (such as arylene, alkylene or alkenylene) incorporated as an integral part of the network. An interesting feature of bridged polysilsesquioxanes is that they may contain a wide range of organic and inorganic ratios without phase separation. The organic group can be varied in length, rigidity, geometry of substitution, and functionality. This wide range of variability offers a chance to investigate how the organic structural unit contributes to bulk properties such as porosity, thermal stability, optical clarity, chemical resistance, and dielectrical constant.

The “star gels” are another family of hybrids. They are derived from polyfunctional network precursors with different flexible arms radiating from a common core and terminating in trialkoxysilane groups (Figure 1.11).

Many other new ormosils have been reported during the last few years but most of them are concerned with synthetic chemistry. The full characterisation and applicability depending on the properties are clearly a task for the future.

1.6.3 Composition of Ormosils.

The combination at the nanosize level of inorganic and organic components in a single material has opened the gates to a new area of materials science. The introduction of organic groups (R) into inorganic networks can be made with two different goals in mind: as network modifiers or as network formers. R will have a modifying effect when it is a simple non-hydrolysable group (e.g., R containing an alkyl group or an organic dye). On the other hand, R will act as a network former if it can react with itself (R containing a vinyl, a methacrylate, or an epoxy group, for example) or additional polymerisable monomers.
A study of recent papers about Ormosils has found plenty of characteristics and properties of these hybrids that can be modulated with the organic content, such as mechanical, optical or electrical properties. The organic content has also influence in porosity control and it can also modify particular chemical or biochemical properties of the ormosil.

On the other hand, the inorganic content has been found to be an important factor to take into account when studying the mechanical and thermal properties of the hybrid. Also it can have some influence on some interesting optical, electrical, electrochemical or magnetic properties.

The final texture of the ormosil is controlled by the kinetics of the different steps of the process: polycondensation, formation of the sol, gelation and ageing. There are many different parameters that can modify the texture of the ormosil during the process, such as purity of the solvent, purity and concentration of the precursors, the temperature, the method of mixing and use of additives.

1.6.4 Properties of Ormosils.

When Schmidt first reported the Ormosils, he was studying different properties of hard contact lenses. Hard contact lenses require mechanical toughness, transparency, oxygen permeability, and wettability of the surface to prevent adhesion of proteins in tears. The presence of dimethylsiloxane and hydroxy groups was found to raise the oxygen permeability and wettability.

Since then, much research has been done in the area of trying to improve certain properties for future devices. The knowledge of structure-property relationships is a powerful tool in designing the synthesis to obtain the desired properties. One point to take into account is how the final structure and morphology of the Ormosil depend on the reaction conditions.
1.6.4.1 Mechanical properties.

The mechanical properties of Ormosils are highly dependent on the texture of the final network. The texture is controlled by some variables of the reaction such as catalyst, leaving groups, size of the organic content, solvent, temperature, concentration and ageing time. Also these parameters are important for the rest of the physical and chemical properties.

One of the systems that has been more developed in order to study the structure of the hybrids is the PDMS-based ormosil. Wilkes and co-workers first reported the PDMS-TEOS system back in 1985. They found that depending on the amount and molecular weight of PDMS in the mixture, the final networks could be either flexible (more organic content) or brittle (the proportion of TEOS is larger).

Mackenzie’s group has also spent a lot of effort describing the properties of this PDMS-TEOS system. They reported the dependence of the mechanical properties of these ormosils on the PDMS content. As the PDMS content increases, hardness (they derived some equations to calculate it from equations of covalent crystals), tensile strength, elastic modulus and brittleness decrease, and toughness and elongation increase. If the PDMS content is over 35% a rubbery ormosil is obtained, which is a promising candidate for high temperature applications. They also have been working on the influence of the temperature on the properties of these PDMS-based ormosils.

Some other research groups have been developing this kind of ormosil from different points of view. An ultrasound-assisted polycondensation of PDMS and TEOS has been used to create sono-ormosils and their structural properties were studied. Dielectric properties of the PDMS:SiO$_2$:TiO$_2$ system have been explored as a function of composition and curing temperature. The influence of the PDMS molecular weight (chain length) on the glass uniformity and mechanical properties has also been investigated.
A new strategy with these hybrids is doping them with metals in order to modify the structural properties. Silver has been added to the network of PDMS-TEOS. It was found that when the silver doped ormosils were exposed to humid air, the samples changed the optical state from transparency to opacity to various degrees depending on the amount of silver incorporation. This phenomenon showed possible applicability as a humidity sensor.

1.6.4.2 Optical properties.

An advantage of using the relatively low temperature sol-gel process is the possibility of obtaining typical optical properties from a glass in a hybrid material. These optical properties and their potential applications are one of the causes of the huge development in these materials in recent years.

The sol-gel derived inorganic oxides are well known for their limited chemical reactivity, but they have other features that make them really interesting such as stability, transparency, they are easy to form into a transparent film, and most importantly, their surface area is very large and their structure highly porous. Organic molecules, on the other hand, have limited thermal stability but they can have a very specific reactivity to a gas, molecule or ion. This reactivity may cause changes in the optical properties of the organic content, which can be detected using simple optical or analytical techniques.

Ormosils have become popular materials for integrated optics applications because they are cheap and they have a readily adjustable composition. Also ormosil films of the required thickness (a few microns) can be deposited in a single step, they can be made photosensitive for direct UV (ultraviolet) writing of waveguides, and their low processing temperatures allows direct integration with semiconductor sources and detectors.

The optical properties can be altered in both linear and non-linear optics by incorporating organic dyes or π-conjugated polymers. Also doping some ormosil films with other organic molecules (two polymethine dyes) can modulate the second order non-linear optical properties.
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A new photorefractive multifunctional ormosil has been developed, which is based on a second-order non-linear optical chromophore and a charge transporting group covalently bound to a silicon atom\textsuperscript{85}. It presents excellent optical quality (single-phase homogeneity) and chemical/environmental stability.

The refractive index has also been modified by changing the organic content of the ormosil. The refractive index can be increased by modifying the silica backbone with phenyl groups, and can be decreased using methyl groups\textsuperscript{71}.

The refractive index is important for photonic applications, but it is not the only requirement. The host ormosil matrix should have a low attenuation in the desired spectral region, reproducible linear optical properties, be mechanically and chemically robust and formable into thin films of about 5 μm thickness\textsuperscript{86}. Some class II ormosils based on non-bridging organic groups (methyl, propyl, vinyl and phenyl) have been structurally investigated for their suitability as photonic materials\textsuperscript{86}.

### 1.6.4.3 Surface properties.

It is widely assumed that as the organic content of ormosil is increased, the average porosity and the surface area of the material changes, leading to a decrease in the matrix rigidity. One of the steps during the sol-gel process has been found determinant in these properties: the ageing process\textsuperscript{87}. The textural properties of the ormosils are mainly controlled by the ageing process. When preparing solids through an ageing process at low temperature and short ageing times, they were found to be microporous with no narrow pore size distribution. On the other hand, increasing the temperature and the length of the ageing produced ormosils with high surface areas and a narrow pore size distribution\textsuperscript{87}.

### 1.6.5 Applications of ormosils.

The person who started to think about possible applications of ormosils was Schmidt back in 1984\textsuperscript{57} when he was searching for a new material for contact lenses. Since then he has contributed more than anybody else in the research of ormosils as useful materials\textsuperscript{56}. Some examples are new contact lenses, scratch resistant coatings, laser
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photopatternable components for optics\textsuperscript{57}, hosts for semiconductor quantum dots, organic dyes and metallic colloids, second order non-linear optically active nanocomposites, Fresnel lenses, photochromic coatings, porous solvent absorbers and GRIN (grating-index-of-refraction) optical components\textsuperscript{56}. Some other possible applications are described in this section.

1.6.5.1 Coatings.

Coating is simply the act of covering a material with a layer with different purposes in mind: to make a substance biocompatible, to increase the thermal, mechanical or chemical stability of a material, to increase wear protection, durability, or lifetime, or to decrease friction or inhibit corrosion\textsuperscript{88}. The material on which the coating is made is called the substrate. The inorganic content of organically modified silicas is based on a Si-O-Si network, and this backbone structure, along with its level of crosslinking, promotes high abrasion resistance. The organic content contributes some other advantages to the coatings, such as improved adhesion between coating and substrate, reduced shrinkage upon curing, and flexibility relative to a pure brittle inorganic sol-gel coating\textsuperscript{89}.

Hard polymethylsiloxanes were developed several decades ago and still have industrial application in improving the abrasion resistance (due to the inorganic structure) of some plastics\textsuperscript{54}. The great mechanical properties due to the inorganic network and their low temperature routes make ormosils very useful for protecting soft materials like transparent glasses (e.g., side windows in buses made from PMMA)\textsuperscript{54}.

Several optically transparent hard coatings with excellent abrasion resistance were obtained when mixing tetraalkoxysilanes with methoxylated urea formaldehyde and methoxylated melamine formaldehyde to form silicone/amine resin hybrids\textsuperscript{90}. These coatings may be used to control the wear of optical plastics such as bisphenol-A polycarbonate and PMMA, which have the potential to replace inorganic glass windows with lower abrasion resistance.
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When the organic modification is a single alkyl chain (hexyl, methyl, ethyl or phenyl), this makes the network hydrophobic, a property which could be interesting for several applications. Phenyl siloxanes can be preferred to the others for their specific properties: high thermal stability\textsuperscript{11}, shift of the glass transition temperature\textsuperscript{11}, and increase of the refractive index\textsuperscript{60}.

The surface reactivity of the ormosil can be controlled by chemical surface modification\textsuperscript{91}. The surface modifier can influence the surrounding molecular structure in a way that thermal and mechanical properties can be influenced.

Making a modification of one of the groups bonded to silicon (Y in figure 1.12) it is possible to create active surfaces in these materials.

\begin{center}
\includegraphics[width=0.3\textwidth]{figure1.12.png}
\end{center}

\textbf{Figure 1.12.} Modification of the surface of ormosils.

With \(Y = -R-NH_2\) (Figure 1.12) it could be easily proved that amino groups act as surface groups both with coatings and porous materials\textsuperscript{57}. The organic content is surrounding the inorganic matrix, modifying the surface of the material. Amino groups can be used as coupling groups for biochemical materials like enzymes or antibodies or as adsorption centres for acids. But it is also possible to incorporate more complicated groups for special purposes (proteins, for example).

\subsection{1.6.5.2 Catalysts and catalyst supports.}

The production of macro-, meso-, and microporous ormosils where the organic content is directing the structure of the hybrid is an area of rapid growth with diverse applications, such as separation technology and catalysis\textsuperscript{92}.

An example of an ormosil acting as a catalyst support is the doping of organically-modified silicas with tetra-\textit{n}-propyl ammonium perruthenate \textit{via} the sol-gel process.
These entrapped species are protected by the surface of the ormosil, yet accessible by external reagents. It was found that the catalyst using the ormosil as catalyst support was 30 times more active in aerobic oxidation of alcohols to carbonyl compounds than that made with conventional SiO₂.

1.6.5.3 Optical applications.
In recent years, ormosils have begun to be interesting because of their integrated optical applications. In comparison with traditional inorganic glasses, ormosils have the potential advantages of lower cost (especially of capital equipment) and readily adjustable composition. Also some ormosil films of the required thickness can be deposited in a single step, and they can be made photosensitive for direct UV writing of waveguides. The relatively low temperatures of the process may enable direct integration with semiconductor sources and detectors. Though the hybrid offers compatibility with the doping agent, some deficiencies of the process will limit some properties and, consequently, some applications. This is the case of residual Si-OH groups contributing to the luminescence quenching of some ions incorporated in the hybrid, with the consequent optical loss phenomena observed in optical waveguide applications.

The possibility of obtaining properties such as fluorescent, photochromic or non-linear optical properties in a solid-state matrix by doping ormosils with dyes makes these ormosils of great interest in the area of optics.

Recently palladium-octa(isopentyl)oxy-phthalocyanine-doped ormosil has been prepared for use as optical limiters, which can protect sensors or human eyes from optical damage by attenuating the intensity of optical beams when the input laser beam exceeds a certain threshold.

Though many new materials have shown interesting properties, commercial applications of these ormosils have not emerged yet.
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1.6.5.4 Sensors.

Ormosils are promising materials for the development of chemical sensors because their organic content can alter the pore size, hydrophobicity, and flexibility of the matrix. Also a specific functional group can be introduced to improve the material performance. The properties of the organic content of the ormosils (such as optical or redox properties) can be exploited for sensor applications. Enzyme or protein doped biosensors also appear to be promising materials. Also sensors for gas detection can be developed using the acid/base characteristics of organic molecules.

On the other hand, the characteristics of the inorganic matrix of the hybrid such as pore size distribution and average, specific surface area, surface polarity, electronic and ionic conductivity, and rigidity, make the hybrids of great importance for sensor applications. The inorganic silica network offers a high photochemical and thermal stability, good optical properties such as transparency in the visible and near ultra-violet domains, rigidity and negligible swelling in liquids, good mechanical properties and sufficient chemical inertness.

The incorporation of a sensing element to detect an analyte or analytes is very easy by the sol-gel approach because of the open porosity. Organic or bio-molecules can be impregnated during this process in order to make sensors. On the other hand, a serious problem for doped sol-gel hybrids is leaching. It occurs when the doped indicator diffuses out of the material and is lost to the surrounding solution. If too much of the indicator is lost, then there may not be enough remaining to provide a measurable response. It has been demonstrated that ormosils can improve the stability of the sensor because of the particular porosity of the matrix, the stabilisation of the dye in the hydrophobic matrix and the specific dye-functional group interactions.

Another way to avoid leaching of the dye is designing of the chemical sensor using organoalkoxysilane that already contains the reagent of interest (Figure 1.13). Because the reagent is covalently attached the to silicate framework, it cannot leach out of the host matrix, the only drawback is that the organoalkoxysilane has to be synthesised.
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Figure 1.13. Structure of an organoalkoxysilane (aminofluorescein derivative) used to produce a pH sensitive indicator.

One of the most promising developments in bio-sensors is that active proteins can be entrapped in sol-gel derived matrices. This discovery is surprising because enzymes are notorious for losing their activity to steric constraints and organic solvent shocks, conditions that are inevitable in sol-gel processing.

One study of an ormosil made of 50% tetramethyl orthosilicate (TMOS) and 50% diphenyl-dimethyl orthosilicate (DiPh-DiMOS) was carried out for use as a sensor for dissolved ammonia. Aminofluorescein was incorporated into such ormosils, producing interesting doped-ormosils because of their permeability to ammonia, impermeability to ions (protons), long operational lifetime and good photostability.

Another different ormosil made with a Pd-linked silane precursor, trimethoxysilane, ferrocene monocarboxylic and HCl (Figure 1.14) was used to encapsulate ferrocene. Its electrochemistry was reversible, so this material is promising for the development of an enzyme electrode or any oxidoreductase-based enzymatic systems.

Figure 1.14. Structure of the suggested Pd-glymo-precursor.
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A halogen anion (Cl', Br', I') sensor was designed by the entrapment of a fluorescent organic molecule, \( N \)-dodecyl-6-methoxyquinolinium iodide (Figure 1.15), in sol-gel silica\(^98\).

![Figure 1.15. \( N \)-dodecyl-6-methoxyquinolinium iodide\(^98\).](image)

The sensing activity is based on a fluorescence quenching mechanism of the quinolinium derivate. The fluorescence intensity of quinine is known to decrease upon addition of halide anions\(^98\).

A pH sensor to monitor the pH in the brain of patients with problems caused by stroke has been developed to provide an indication of brain tissue variability\(^103\). The sensor uses a self referencing dye, seminaphthorhodamine-1-carboxylate (SNARF-1C) (Figure 1.16), encapsulated within a sol-gel matrix formed with TMOS. Once encapsulated, leaching of the dye out of the matrix was found to be very low, which is very important for any type of sensor but especially for those proposed for use in vivo.

![Figure 1.16. Chemical structure of SNARF-1C\(^103\).](image)

The pK\(_a\) of 7.4 makes SNARF-1C ideal for blood pH measurements. Using luminescence spectrometry two spectrally distinguishable forms can be found: the acid form with an
emission peak at approximately 580 nm, and the base form with an emission peak at
approximately 640 nm\textsuperscript{103}.

1.6.5.5 Laser applications.
An ornosil must satisfy three important criteria for organic-inorganic hybrid laser host
materials\textsuperscript{94}: an optically transparent matrix with little or no phase separation; comparable
volume fractions of organic and inorganic components to obtain the benefits of both
phases; and a high degree of polymerisation reaction.

Methyl modified silicates show many of the characteristics required of host materials for
solid state dye lasers\textsuperscript{104}. They can be processed in a relatively short time and polished by
conventional glass polishing methods. The light scattering in these materials is
reasonably low with no detectable phase separation.

Different doping agents have been used, and some of them, e.g. a new laser dye
\(1,3,5,7,8\)-pentamethylpyrromethene-2,6-disulphonate-BF\(_3\) complex\textsuperscript{105}, have been found
to have a high efficiency and a long lifetime in a compact new laser device.

1.6.5.6 Photorefractive materials.
A new photorefractive multifunctional ormosil has been developed\textsuperscript{85}. This ormosil
consists of a second-order non-linear optical chromophore and a charge-transporting
group covalently bound to a silicon atom. It exhibits electro-optic and charge transporting
properties. When it is doped with a photocharge generation sensitizer, the material shows
photorefractivity, with excellent optical quality (single-phase homogeneity), and
chemical/environmental stability\textsuperscript{85}.

1.6.5.7 Dental restorative materials.
Traditionally the materials that have been used as dental restorative materials are acrylate
monomers (the source of resin) mixed with silica (filler material). The major problems of
these materials are lack of adhesion and shrinkage of the resin during polymerisation (the
shrinkage does not allow the formation of an adhesive bond between the resin and the
dentine). Using metal alkoxides (e.g. orthosilicate) with the monomer attached to them during the sol-gel process minimises the shrinkage problem, and the use of a hydrophilic group (such as -OH, -SH or -NH₂) may improve the adhesion of the dentine to the resin.

1.6.5.8 Bioencapsulation.

The fact that the organic content of ormosils can incorporate a variety of biologically friendly groups such as amino, amido, carboxy, hydroxy, thiol, and mixed functionalities as well as redox-active metallocenes, nicotinamides, flavins, and quinines, makes them ideal candidates for bioencapsulation. Also the matrices of the ormosils offer tailorable hydrophilic, hydrophobic, ionic and H-bonding capacities as well as electrochemical activities, together with good porosities. The most researched area has been the bioencapsulation of biosensors, but also other materials like proteins, and biocatalysts have been encapsulated by ormosils.

1.6.5.9 Bioactive ormosils.

Bioactive ceramics containing CaO and SiO₂ as main ingredients can bond to living bone with an intervening apatite layer deposited on their surface when they are embedded in the body. Organically modified silicate gels have been produced from PDMS-TEOS-Ca(NO₃)₂.4H₂O solutions. Different combinations of the components were tested, finding out that one of them can deposit apatite within 3 days soaking in the simulated body fluid (SBF) because it included many calcium ions on the surface.

1.6.6 Ormosils via the non-hydrolytic sol-gel route.

Though the hydrolytic sol-gel process has been widely investigated for the synthesis of ormosils in the last 20 years, the non-hydrolytic route to produce ormosils has been researched only in the last few years mainly by two groups in Surrey (UK) and Montpellier (France) independently.

In the University of Surrey (UK), the non-hydrolytic sol-gel route to inorganic oxides had been extended to the preparation of hybrid ormosils with a variety of
organic groups\textsuperscript{110,111}. The process was based on the polycondensation of alkylchlorosilanes with oxygen donors such as alkoxysilanes (Equation 1.16) or alkylalkoxysilanes (Equation 1.17). The precursors were already organically modified and commercially available.

\[
\text{RSiCl}_3 + 0.75\text{Si(OR')}_4 \rightarrow \left[\text{RSi}_{1.75}\text{O}_3\right]_n + 3\text{R'Cl} \quad (1.16)
\]

\[
\text{RSiCl}_3 + \text{RSi(OR')}_3 \rightarrow \left[\text{R}_2\text{Si}_2\text{O}_3\right]_n + 3\text{R'Cl} \quad (1.17)
\]

When only one of the precursors has an alkyl modification (Equation 1.16), an ormosil with only one type of modifying group is obtained (in this ormosil not every silicon centre is attached to an organic group). On the other hand, when both precursors are organically modified (Equation 1.17), a silsesquioxane (in this type of ormosil, every silicon atom is attached to an organic moiety) that can contain two different organic groups is obtained. Different organic groups such as alkyl (from methyl to decyl chains), vinyl or aryl have been used in both cases. Because the precursors were liquid, it was not necessary to use solvents. As in the case of silicon oxide\textsuperscript{16}, the reaction was found to work using iron(III) chloride as catalyst. Previous works with the non-hydrolytic route were carried out using sealed tubes, but during this work, the reactions were performed under flowing nitrogen\textsuperscript{111}. An alkyl (methyl or ethyl) chloride was obtained as by-product, but it is gaseous under ambient temperature and it was assumed to be removed by the nitrogen flow during the reaction\textsuperscript{111}.

The ormosils obtained through this approach were found to have relatively low surface area, but when thermal degradation of the organic component was carried out, high surface area was found in the resultant silicon oxide\textsuperscript{111}.

The work at Université Montpellier II using the non-hydrolytic sol-gel route to obtain ormosils was based on the synthesis of different silsesquioxanes\textsuperscript{112}. Methyl-, vinyl- and octadecylsilsesquioxane gels were obtained in a solvent-free condensation of alkyltrichlorosilane with different oxygen donors, such as iso-propylether, ethyl ether (Equation 1.18) or methyltriethoxysilane\textsuperscript{112}.
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\[ 2\text{RSiCl}_3 + 3\text{R}^*_2\text{O} \rightarrow [\text{R}_2\text{Si}_2\text{O}_3]_n + 6\text{R}'\text{Cl} \] (1.18)

Also different metal chlorides as catalysts were tested for the condensation process, and the efficiency was found to decrease in the order FeCl$_3$ > ZrCl$_4$ > AlCl$_3$ > TiCl$_4$ >> BCl$_3$.112

Both groups were using the same condensation process, but different experimental conditions were used during the reaction. Whilst the Surrey group was using a flowing nitrogen system at atmospheric pressure, the Montpelier group employed sealed tubes under autogeneous pressure. During the reactions with the sealed tubes, pure phenylsilsesquioxane gels could not be obtained because the by-product of the reaction (alkyl chloride) may produce some C-Si bond cleavage in the phenyl-silicon atom bond.112 That demonstrates that the selection of the experimental conditions is going to have a strong effect on the final properties of the material. Thus, two chemically identical products can have different properties depending on the experimental conditions of the process.55

The gel time of the process was analysed by both groups, and a combination of different factors such as statistical (less functionality on the silicon centres), electronic and steric factors were found to govern the effect of the organic content of the ormosils on the gel time.55

During the synthesis of similar ormosils using the hydrolytic sol-gel route, two separate phases were found when condensing octyltriethoxysilane with tetramethyl orthosilicate at a higher ratio of 1:6.113 This phase separation was avoided using the non-hydrolytic route where long alkyl chains were used as the organic content of the ormosils.111 This is an example where the non-hydrolytic route resolves a problem that occurred when using the hydrolytic sol-gel process.
1.6.7 Future of sol-gel ormosils.

More than four dozen leaders of the sol-gel community were asked about the future of ormosils, and they cited ormosils as materials which cannot be achieved by other methods, such as films and coatings with low temperature processing, with a range of new functions which cannot be achieved for materials with homogeneous microstructures\textsuperscript{114}.

The same survey showed what the scientific community thinks is going to be the major application of these materials. More than half of the respondents replied that ormosils will be mainly used as hard and abrasion resistant-coatings on plastics. 16\% said as nanocomposites and protective coatings, followed by 12\% that thought as coated windshields. One out of four respondents cited ormosils as future materials for optical, chemical and biological applications, optical materials, optical coatings, antireflection coatings, optical components, photochromic coatings, smart materials, sensors, antiadhesion coatings, easy-to-clean coatings, corrosion-resistant coatings, high temperature rubbers and thick (multimicron) films\textsuperscript{114}.
1.7 References


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Chapter 2

Non-hydrolytic sol-gel synthesis of ormosils
Chapter 2: Non-hydrolytic sol-gel synthesis of ormosils

2.1 Introduction.

The method used to synthesise the ormosil materials was the non-hydrolytic sol-gel route to oxides previously reported but using alkyl modified precursors (alkyl chlorosilanes). The reaction is based on the direct polycondensation of TEOS with different alkyltrichlorosilanes (methyl-, ethyl-, hexyl- and phenyltrichlorosilane) using iron(III) chloride as catalyst (Equation 2.1).

\[
\text{RSiCl}_3 + 0.75\text{Si(OEt)}_4 \rightarrow [\text{RSi}_{1.75}\text{O}_3]_n + 3\text{EtCl} \quad (R=\text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_{13}, \text{C}_6\text{H}_5)
\] (2.1)

In the past, the synthesis of these ormosils was carried out in an uncontrolled way. In the present work the production of controlled morphology particles has been targeted under 'pseudo dispersion polymerisation' conditions. The first part of the investigation involved the search for the optimal conditions for the reaction trying different solvent mixtures, stirring methods and speed, and effects of different additives (surfactants and polystyrene).

2.2 Experimental.

2.2.1 Materials.

Methyltrichlorosilane (MTCS) 99 %, ethyltrichlorosilane (ETCS) 99 %, phenyltrichlorosilane (PTCS) 97 %, hexyltrichlorosilane (HTCS) 97 %, silicon tetrachloride 99.9 %, diethyl ether 99.9 %, polyoxyethylene 4-lauryl ether (Brij® 30) \( M_n \) ca. 362, polyoxyethylene 2-cetyl ether (Brij® 52) \( M_n \) ca. 330, polyoxyethylene 20-oleyl ether (Brij® 98) \( M_n \) ca. 1,150, polyoxyethylene 2-oleyl ether (Brij® 92) \( M_n \) ca. 357, polyoxyethylene 2-nonylphenyl ether (Igepal® co-210) \( M_n \) ca. 308, polystyrene (\( M_n \) ca. 45,000) and polystyrene (\( M_n \) ca. 1,000,000) (Aldrich) were all used as received. Tetraethyl orthosilicate (TEOS) (Lancaster) 98 % and iron(III) chloride (BDH) 98 % were used as received. Dimethyl sulfoxide (DMSO) (Aldrich) 99.9 % was dried with 4Å molecular sieves which were activated by heating in an oven at 100°C for 4 hours.

The solvents petroleum ether (boiling fraction 100-120°C) (Fisher Scientific) and toluene low in sulfur (Fisher Scientific) 99.5 % were dried before used. Toluene was distilled
from Na (metal) + benzophenone under an atmosphere of N₂ (g) and petroleum ether was
dried using molecular sieves.

Many of the precursors used (silicon chlorides) are very reactive. Air-sensitive liquid
reactants (RSiCl₃) were introduced to the reaction system from a syringe via a septum.

2.2.2 Instrumentation.

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer 2000 FT-IR
spectrophotometer interfaced with a Perkin-Elmer computer (PE-Spectrum v2.00
software was used). Samples were ground with potassium bromide, KBr, and pressed as a
pellet for 15 minutes under a constant pressure of 10 tons. IR spectra were measured on
undiluted samples with a resolution of 4 cm⁻¹ and 16 scans. Abbreviations used to
describe absorptions are as follows: vs= very strong; s= strong; m= medium; w= weak;
vw= very weak; b= broad; sp= sharp and sh= shoulder.

Elemental analyses were kindly carried out by Ms Nicola Walker at the University of
Surrey on a Leeman Laboratories Inc. CE 440 Elemental Analyser.

Surface morphology was evaluated using a Hitachi S-3200 Variable Pressure Scanning
Electron Microscope. Prior to mounting, specimens were gold coated using an Edwards
Gold Sputter Coating unit to prevent charging under the electron beam.

²⁹Si NMR analyses were kindly carried out by Dr David Apperley at the University of
Durham. Solid-state ²⁹Si cross-polarised (CP) and direct-polarised (DP) NMR
spectroscopies were performed at ambient temperature on a Varian UNITYInova
spectrometer with a 7.05 T Oxford Instruments magnet. Spectra were recorded against
external tetramethylsilane (TMS) with magic angle spinning (MAS). Details of the
instruments conditions are given on each spectrum. Tetrafunctional silicon centres were
named with the conventional Qⁿ notation where Q refers to (SiO)ₙSi(OR)₄₋ₙ units where
n is the number of bridging oxygen atoms surrounding the central silicon atom.
Trifunctional silicon centres were named with the conventional Tⁿ notation where T
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refers to \((\text{SiO})_n\text{R'}\text{Si(OR)}_{3-n}\) units where \(n\) is the number of bridging oxygen atoms surrounding the central silicon atom.

Some reactions were stirred using an ULTRA TURRAX® T 25, which is a dispersion unit; in connexion with a dispersion tool, it manufactures emulsions and dispersions.

2.2.3 Procedure.

2.2.3.1 Non-hydrolytic sol-gel synthesis of ormosils using different solvents.

In a typical experiment, the methyl-modified silica \((\text{CH}_3\text{Si}_{1.75}\text{O}_3, \text{exp. no. 8})\) was formed by reacting MTCS \((3.89 \text{ g, } 26 \text{ mmol})\) with TEOS \((4.00 \text{ g, } 19 \text{ mmol})\) in the presence of iron(III) chloride catalyst \((0.08 \text{ g, } 1 \text{ wt. % based on weight of reactants})\), using a mixture of toluene \((4.5 \text{ ml})\) and petroleum ether \((100-120°C) \ (13.5 \text{ ml})\) as the solvent. The reaction was carried out under nitrogen flow. A mechanical stirrer was used during the reaction. The mixture was stirred at room temperature for 2 hours, and then the temperature was increased to reflux temperature \((110°C)\). The reaction was kept under these conditions for 20 hours. The resulting solid was filtered and washed with diethyl ether. The obtained solid was dried in a vacuum oven at 60°C for 8 hours to yield a dark powder \((2.89 \text{ g, } 99 \%)\).

Elemental analysis gave C, 12.1; H, 3.29 % (calculated: C, 10.7; H, 2.67 %). The FT-IR spectrum showed absorptions at: \(\nu_{\text{max.}} \ (\text{cm}^{-1})\): 3650-3050 (w, b); 2970-2950 (w, sp); 1630-1610 (w, b); 1390 (vw); 1275 (s, sp); 1010 (vs, sp); 824 (s, sh); 775 (vs, sp); and 590-510 (s, b).

2.2.3.2 Non-hydrolytic sol-gel synthesis of ormosils using different stirring methods.

In a typical experiment with the ULTRA TURRAX® T25 (high-speed dispersing and emulsifying unit), the methyl-modified silica \((\text{CH}_3\text{Si}_{1.75}\text{O}_3, \text{exp. no. 11})\) was produced by reacting MTCS \((3.89 \text{ g, } 26 \text{ mmol})\) with TEOS \((4.00 \text{ g, } 19 \text{ mmol})\) in the presence of
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iron(III) chloride catalyst (0.1 g, 1.3 wt. % based on weight of reactants), using a mixture of toluene (4.5 ml) and petroleum ether (100-120°C) (13.5 ml) as the solvent under nitrogen flow.

The stirring speed was 8000 rev./min at room temperature for 2 hours, then increased to 9500 rev./min for 1 hour. The temperature was then increased to 110°C and maintained for 3 hours under stirring (9500 rev./min). The temperature was decreased to room temperature over 1 hour and the stirring speed set at 8000 rev./min for a further hour. The obtained grey particles were filtered and washed with ether, yielding a dark powder, which was dried in a vacuum oven at 60°C for 8 hours. The yield was 2.41 g (21.5 mmol, 83 %).

Elemental analysis gave: C, 12.9; H, 3.70 % (calc.: C, 10.7; H, 2.67 %). The FT-IR spectrum showed the characteristic intense, sharp band of the symmetric methyl deformation from Si-CH₃ at 1274 cm⁻¹. The asymmetric stretching vibrations of Si-O-Si were also present at 1019 cm⁻¹.

2.2.3.3 Non-hydrolytic sol-gel synthesis of ormosils using different surfactants as additives.

In a typical experiment, the hexyl-modified silica (HexSi₁.₇₅O₃, exp. no. 22) was obtained by reacting HTCS (5.62 g, 26 mmol) with TEOS (4.00 g, 19 mmol) in the presence of iron(III) chloride (0.1 g, 1 wt. % based on weight of reactants) and Igepal® co-210 (0.48 g, 5 wt. % based on weight of reactants) as surfactant under nitrogen flow. A mixture of toluene (4.5 ml) and petroleum ether (100-120°C) (13.5 ml) was used as the solvent.

The reaction was started at room temperature for 2 hours under mechanical stirring, and then the temperature was increased to reflux temperature (110°C). The reaction was kept under these conditions for 21 hours. The resulting product was filtered and washed with diethyl ether. The obtained solid was dried in a vacuum oven at 60°C for 8 hours to yield a black rubbery precipitate (2.43 g, 12.8 mmol, 49 %).
Elemental analysis gave: C, 44.3; H, 7.94 % (calc.: C, 39.5; H, 7.14 %). The FT-IR spectrum showed absorptions at: $v_{\text{max}}$ (cm$^{-1}$): 2952 (m, sp); 2925 (s, sp); 2857 (m, sp); 1509 (m, sp); 1456 (m, sp); 1179 (s, sh); 1007 (vs, sp); 961 (s, sh); 831 (s, sp); 794 (s, sp); 717 (s, sp); 682 (s, sp); 600 (s, b).

**2.2.3.4 Non-hydrolytic sol-gel synthesis of ormosils dispersing the sol in water.**

The methyl-modified silica sol (exp. no. 27) was formed by reacting MTCS (3.89 g, 26 mmol) with TEOS (4.0 g, 19 mmol) in the presence of iron(III) chloride catalyst (0.1 g, 1.3 wt. % based on weight of reactants) and surfactant Brij® 52 (0.39 g, 5 wt. % based on weight of reactants), and using a mixture of toluene (4.5 ml) and petroleum ether (100-120°C) (13.5 ml) as the solvent under nitrogen flow. All the components were mixed at room temperature over 2 hours using a mechanical stirrer. After that, the temperature was increased to 110°C and the reflux was maintained for 20 hours under continuous stirring. The temperature was then decreased to room temperature over 1 hour and the mechanical stirrer was maintained. The obtained sol was then dispersed in water with the Ultra Turrax® high speed stirrer during 15 minutes at 9500 rev./min. The obtained grey gel was filtered and washed with ether, and then dried in a vacuum oven at 60°C for 48 hours. The yield was 34 % (1.00 g, 8.92 mmol).

Elemental analysis gave: C, 18.3; H, 4.16 % (calc.: C, 10.6; H, 2.67 %). The FT-IR spectrum showed absorptions at: $v_{\text{max}}$ (cm$^{-1}$): 2952 (w, sp); 2919 (w, sp); 2874 (w, sp); 1271 (s, sp); 1097 (vs, sh); 1019 (vs, sp); 940 (s, sh); 818 (s, sh); 769 (vs, sp); 560 (s, b).

**2.2.3.5 Non-hydrolytic sol-gel synthesis of silicon dioxide under typical conditions.**

Silicon tetrachloride (4.42 g, 26 mmol) was mixed with TEOS (5.41 g, 26 mmol) in the presence of iron(III) chloride (0.1 g, 1 wt. % based on weight of reactants) acting as the catalyst of the reaction (exp. no. 34). The usual combination of toluene (4.5 ml) with
petroleum ether (100-120°C) (13.5 ml) was used as solvent. The reaction (Equation 2.2) was carried out under nitrogen flow.

\[
\text{SiCl}_4 + \text{Si(OC}_2\text{H}_5)_4 \rightarrow 2\text{SiO}_2 + 4\text{EtCl}
\] (2.2)

As usual, the reaction was stirred at room temperature for 1 hour with a mechanical stirrer. The temperature was then increased to 110°C and maintained for 19 hours under stirring. The temperature was decreased to room temperature over 1 hour keeping the stirring. The obtained product was filtered and washed with ether, and then dried for 48 hours at 60°C in a vacuum oven. Silicon dioxide (2.80 g) was obtained (46.6 mmol, 90%).

The FT-IR spectrum showed absorptions at: \(\nu_{\text{max.}}\) (\(\text{cm}^{-1}\)): 1125 (s, sh); 1040 (vs, sp); 933 (s, sh); 812 (s, sh); 648 (m, b); 611 (m, sp); 580 (m, sp); 507 (m, sp).

2.2.3.6 Non-hydrolytic sol-gel synthesis of ormosils using polystyrene as an additive.

In a typical experiment using polystyrene as additive, the hexyl-modified silica (exp. no. 35) was obtained by reacting HTCS (5.62 g, 26 mmol) with TEOS (4.00 g, 19 mmol) in the presence of iron(III) chloride catalyst (0.1 g, 1 wt. % based on weight of reactants) and polystyrene (\(M_n\ ca. 45,000\)) (0.48 g, 5 wt. % based on weight of reactants) as additive, using a mixture of toluene (4.5 ml) with petroleum ether (100-120°C) (13.5 ml) as the solvent under nitrogen flow.

The process was started by stirring the mixture at room temperature for 2 hours, and then the temperature was increased to 110°C and maintained for 20 hours under stirring. Then the temperature was decreased to room temperature and maintained for 2 hours stirring. The obtained product was then filtered and washed with ether. The solid was dried in a vacuum oven at 60°C for 48 hours. The amount of hexyl-modified silica obtained was 3.52 g (19.3 mmol, 74%).
Elemental analysis gave: C, 42.4; H, 7.27 % (calc.: C, 39.5; H, 7.14 %). The FT-IR spectrum showed absorptions at: $v_{\text{max}}$ (cm$^{-1}$): 2953 (m, sp); 2924 (s, sp); 2854 (m, sp); 1451 (m, sp); 1178 (s, sh); 1088 (s, sh); 1010 (vs, sp); 960 (s, sh); 842 (s, sp); 794 (s, sp); 756 (s, sh); 693 (s, sp); 598 (s, b).

2.2.3.1 Non-hydrolytic sol-gel synthesis of silsesquioxanes using DMSO as the oxygen donor.

In a typical experiment, methyl-silsesquioxane ($\text{Me}_2\text{Si}_{203} \text{n}$ (exp. no. 42) was formed by reacting MTCS (3.89 g, 26 mmol) with DMSO (25 ml), which is acting as the oxygen donor in the condensation and solvent at the same time, under nitrogen flow. The silicon chloride was added to the DMSO using a syringe pump at a rate of 20 ml/hour due to the very exothermic reaction produced. Equation 2.3 shows the idealised reaction:

$$2\text{RSiCl}_3 + 3\text{OS(CH}_3\text{)_2} \rightarrow \text{R}_2\text{Si}_{203} + 3\text{CH}_3\text{SCH}_2\text{Cl} + 3\text{HCl} \quad (2.3)$$

The colloidal solution was stirred with an overhead stirrer for 2 hours at room temperature. After that time a white sol was obtained. After filtration, the white powder was washed with water to eliminate DMSO impurities within the network of the silsesquioxane. This washing was done by dispersing the obtained solid in 1 litre of water under magnetic stirring for 10 hours (overnight) and then the product was filtered; this operation was repeated twice. The obtained material was dried in vacuum oven at 80°C for 8 hours, and 1.40 g of methyl-silsesquioxane was obtained (80 % yield).

Elemental analysis gave: C, 14.9; H, 4.83 % (calc.: C, 17.9; H, 4.48 %). The FT-IR spectrum showed absorptions at: $v_{\text{max}}$ (cm$^{-1}$): 2972 (w, sp); 1409 (vw); 1271 (s, sp); 1041 (vs, sh); 988 (vs, sp); 857 (s, sp); 762 (vs, sp); 669 (s, b); 605-540 (s, b).

2.2.3.8 Non-hydrolytic sol-gel synthesis of silicon dioxide using DMSO as the oxygen donor.

The synthesis of silicon dioxide was carried out under similar conditions to those for the previous silsesquioxanes (see section 2.2.3.7). Reacting DMSO (25 ml) with silicon
tetrachloride (4.42 g, 26 mmol) under nitrogen flow, a white sol was obtained (Equation 2.4). Silicon halide was added through a syringe to the solution of DMSO at a rate of 20 ml/hour.

\[
\text{SiCl}_4 + 2\text{OS(CH}_3\text{)}_2 \rightarrow \text{SiO}_2 + 2\text{CH}_3\text{SCH}_2\text{Cl} + 2\text{HCl} \quad (2.4)
\]

The colloidal solution was stirred with an overhead stirrer for 2 hours at room temperature. Then the obtained product was washed with water as before (see section 2.2.3.7) to remove the DMSO from the solid. 0.69 g (44 %) of silicon dioxide was obtained after drying the product for 8 hours at 80°C in a vacuum oven.

The FT-IR spectrum showed absorptions at: \(\nu_{\text{max.}} \, (\text{cm}^{-1})\): 3500-3000 (vw, b); 1680 (s, sp); 1385 (vw); 1118 (s, sh); 1039 (vs, sp); 942 (s, sp); 792 (s, sp).

2.3 Results and discussion.

2.3.1 Non-hydrolytic sol-gel synthesis of ormosils using different solvents.

In the past, the non-hydrolytic sol-gel process has been used for the synthesis of ormosils in the absence of solvents\(^4,5\). However, the use of a solvent potentially offers some control over the product morphology. The solvent was carefully selected so that the precursors were soluble at the start of the reaction, with the ormosil precipitating out as the reaction progresses. Because of the totally opposed polarities of the organic content (alkyl or aryl substituents) and the silica network, it was thought that the process may behave like a dispersion polymerisation, with the organic groups projecting into the non-polar solvent, and the inorganic polar silica forming the core of the resulting particles. Spherical particles were expected to be formed as a result of the steric stabilisation of these particles.

Different solvents were tested during the first part of the work, including various mixtures of toluene and petroleum ether (100-120°C). The results of the experiments are shown in table 2.1:
Table 2.1. Results of non-hydrolytic sol-gel synthesis of ormosils using different solvents.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Oxygen donor</th>
<th>Temp. (°C)</th>
<th>Reaction time (hours)</th>
<th>Product</th>
<th>Comments and appearance</th>
<th>FTIR absorptions (cm⁻¹)</th>
<th>Elemental analysis</th>
<th>Yields</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>FeCl₃</td>
<td>Si(OC₂H₅)₄</td>
<td>110</td>
<td>24</td>
<td>Dark green precipitate</td>
<td>1560-3000 (m, s) 2955 (s, w) 2855 (s, m) 1600-1750 (m, vs) 1450 (m, m) 1072 (s, s)</td>
<td>C.1.3.2.3.4</td>
<td>3.06%</td>
<td>84%</td>
<td>a. Percentages based on weights of MTCS + TEOS.</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>FeCl₃</td>
<td>Si(OC₂H₅)₄</td>
<td>110</td>
<td>24</td>
<td>Dark green precipitate</td>
<td>1560-3000 (m, s) 2955 (s, w) 2855 (s, m) 1600-1750 (m, vs) 1450 (m, m) 1072 (s, s)</td>
<td>C.1.3.2.3.4</td>
<td>3.06%</td>
<td>84%</td>
<td>a. Percentages based on weights of ETCS + TEOS.</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>FeCl₃</td>
<td>Si(OC₂H₅)₄</td>
<td>110</td>
<td>24</td>
<td>Dark green precipitate</td>
<td>1560-3000 (m, s) 2955 (s, w) 2855 (s, m) 1600-1750 (m, vs) 1450 (m, m) 1072 (s, s)</td>
<td>C.1.3.2.3.4</td>
<td>3.06%</td>
<td>84%</td>
<td>a. Percentages based on weights of HTCS + TEOS.</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>FeCl₃</td>
<td>Si(OC₂H₅)₄</td>
<td>110</td>
<td>24</td>
<td>Dark green precipitate</td>
<td>1560-3000 (m, s) 2955 (s, w) 2855 (s, m) 1600-1750 (m, vs) 1450 (m, m) 1072 (s, s)</td>
<td>C.1.3.2.3.4</td>
<td>3.06%</td>
<td>84%</td>
<td>a. Percentages based on weights of PTCS + TEOS.</td>
</tr>
</tbody>
</table>

a. Percentages based on weights of MTCS + TEOS.
b. Percentages based on weights of ETCS + TEOS.
c. Percentages based on weights of HTCS + TEOS.
d. Percentages based on weights of PTCS + TEOS.
e. Yields were calculated based on the theoretical formula of the product.
<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Alkyl-trichlorosilane</th>
<th>Oxygen donor</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Reaction time</th>
<th>Temp.</th>
<th>Comments and appearance</th>
<th>Yield</th>
<th>IR absorptions (cm(^{-1})) (approximate)</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>HexSiCl(_3) (5.62 g, 26 mmol)</td>
<td>Si(OE)(_4) (4.00 g, 19 mmol)</td>
<td>FeCl(_3) (0.1g, 1 wt.%)</td>
<td>toluene (1.35 mL) + petroleum ether (4.5 mL)</td>
<td>24 hour</td>
<td>110°C</td>
<td>Dark precipitate</td>
<td>104%</td>
<td>3550-3200 (w,b); 2950 (s, sp); 2920 (s, sp); 2855 (s, sp); 1650-1590 (w, b); 1457 (m, sp); 1180 (s, sh); 1005 (vs, sp); 960 (s, sh); 840 (s, sp); 790 (s, sp); 690 (s, sp); 620-550 (s, b)</td>
<td>C, 37.8; H, 7.57% (calc: C, 39.5; H, 7.14%)</td>
</tr>
<tr>
<td>6</td>
<td>HexSiCl(_3) (5.62 g, 26 mmol)</td>
<td>Si(OE)(_4) (4.00 g, 19 mmol)</td>
<td>FeCl(_3) (0.1g, 1 wt.%)</td>
<td>toluene (9.0 mL) + petroleum ether (9.0 mL)</td>
<td>24 hour</td>
<td>110°C</td>
<td>Dark precipitate</td>
<td>90%</td>
<td>3550-3150 (w, b); 2950 (s, sp); 2920 (s, sp); 2855 (s, sp); 1660-1590 (w, b); 1456 (m, sp); 1179 (s, sh); 1007 (vs, sp); 960 (s, sh); 840 (s, sp); 784 (s, sp); 681 (s, sp); 620-540 (s, b)</td>
<td>C, 37.1; H, 7.34% (calc: C, 39.5; H, 7.14%)</td>
</tr>
<tr>
<td>7</td>
<td>HexSiCl(_3) (5.62 g, 26 mmol)</td>
<td>Si(OE)(_4) (4.00 g, 19 mmol)</td>
<td>FeCl(_3) (0.1g, 1 wt.%)</td>
<td>toluene (4.5 mL) + petroleum ether (1.35 mL)</td>
<td>24 hour</td>
<td>110°C</td>
<td>Dark precipitate</td>
<td>104%</td>
<td>3560-3190 (w, b); 2952 (s, sp); 2929 (s, sp); 2859 (s, sp); 1635-1580 (w, b); 1466 (m, sp); 1176 (s, sh); 1006 (vs, sp); 958 (s, sh); 839 (s, sp); 796 (s, sp); 686 (s, sp); 615-830 (s, b)</td>
<td>C, 38.2; H, 7.55% (calc: C, 39.5; H, 7.14%)</td>
</tr>
<tr>
<td>8</td>
<td>MeSiCl(_3) (3.89 g, 26 mmol)</td>
<td>Si(OE)(_4) (4.00 g, 19 mmol)</td>
<td>FeCl(_3) (0.08 g, 1 wt.%)</td>
<td>toluene (4.5 mL) + petroleum ether (1.35 mL)</td>
<td>20 hour</td>
<td>110°C</td>
<td>Dark precipitate</td>
<td>99%</td>
<td>3650-3050 (w, b); 2970-2950 (w, sp); 1630-1610 (w, b); 1390 (wv); 1275 (s, sp); 1010 (vs, sp); 824 (s, sh); 775 (vs, sp); 590-510 (s, w)</td>
<td>C, 12.1; H, 3.29% (calc: C, 10.7; H, 2.67%)</td>
</tr>
<tr>
<td>9</td>
<td>EtSiCl(_3) (4.25 g, 26 mmol)</td>
<td>Si(OE)(_4) (4.00 g, 19 mmol)</td>
<td>FeCl(_3) (0.08 g, 1 wt.%)</td>
<td>toluene (4.5 mL) + petroleum ether (1.35 mL)</td>
<td>21 hour</td>
<td>110°C</td>
<td>Dark precipitate</td>
<td>101%</td>
<td>3530-3270 (wv, b); 2966 (m, sp); 2922 (m, sp); 2884 (m, sp); 1616 (wv, b); 1460 (m, sp); 1254 (s, sp); 994 (vs, sh); 1030 (vs, sp); 954 (vs, sh); 842 (s, sp); 750 (s, sp); 591 (s, sp); 615-540 (s, b)</td>
<td>C, 19.6; H, 4.61% (calc: C, 19.0; H, 3.96%)</td>
</tr>
<tr>
<td>10</td>
<td>PrSiCl(_3) (5.50 g, 26 mmol)</td>
<td>Si(OE)(_4) (4.00 g, 19 mmol)</td>
<td>FeCl(_3) (0.1g, 1 wt.%)</td>
<td>toluene (4.5 mL) + petroleum ether (1.35 mL)</td>
<td>21 hour</td>
<td>110°C</td>
<td>Dark precipitate</td>
<td>90%</td>
<td>3650-3150 (wv, b); 1595 (m, sp); 1431 (m, sp); 1131 (vs, sh); 1077 (vs, sp); 956 (vs, sp); 845 (m, sh); 790 (s, sp); 756 (s, sp); 656 (vs, sp); 650-540 (s, b)</td>
<td>C, 35.7; H, 3.26% (calc: C, 41.3; H, 2.87%)</td>
</tr>
</tbody>
</table>
Chapter 2: Non-hydrolytic sol-gel synthesis of ormosils

During the process ethyl chloride is produced as by-product (Equation 2.1), which is gaseous under ambient conditions, so it was assumed to be removed in the nitrogen flow during the reaction.

Quite good yields were obtained in all reactions and the elemental analysis figures were obtained in approximate agreement with the theoretical values; in some cases the yield was over 100 % (experiments 1, 5, 7 and 9). It is assumed that it could be due to two main reasons: there is still some solvent present in the product, as it can be seen in the IR spectrum of exp. no. 5 (Figure 2.1). A broad absorption between 3550 and 3200 cm\(^{-1}\) together with the absorption at approx. 1600 cm\(^{-1}\) (aromatic zone) shows that there is still some toluene present on the product, even after drying it for 8 hours in a vacuum oven at 60°C. The second reason for the high yield could be due to incomplete reactions, being present some starting material and/or some oligomers. Si-O-Et stretching vibrations are present in the 1110-1000 cm\(^{-1}\) range, but because siloxane is present in the sample, these bands are masked. Other characteristic absorptions of Si-O-Et groups are at approx. 970-940 cm\(^{-1}\), and in this area (at 960 cm\(^{-1}\)) a strong absorption can be seen (Figure 2.1) as a shoulder of the strong Si-O-Si absorption at 1005 cm\(^{-1}\), so some oligomers (or starting material) may still be present in the product.

![Figure 2.1. IR spectrum of HexSi\(_{1.75}\)O\(_3\) synthesised using a mixture of solvents (toluene:petroleum ether 75:25 volume %) (exp. no. 5).](image)
Chapter 2: Non-hydrolytic sol-gel synthesis of ormosils

In the first set of experiments (experiments 1-4), toluene was used as the solvent to maximise the interaction between the organic content and the catalyst and also to stabilise the dispersion, which is produced because of the different polarities of the organic content of the hybrid and the silica network. Toluene was found to be a good solvent to dissolve the catalyst (iron(III) chloride).

The organic content of the ormosil was found to play an important role in the morphology of the hybrid, which was evaluated using Scanning Electron Microscopy (SEM). When the organic moiety is an alkyl group (methyl, ethyl or hexyl), aggregated, irregular particles of diameter between 5 and 50 μm were obtained (Figure 2.2, left picture). On the other hand, when the organic content of the ormosil is an aryl group (phenyl), bigger particles (diameter > 100 μm) of irregular shape were produced (Figure 2.2, right picture). However, it could be the case that these big particles are made up of smaller particles that have aggregated to produce a smooth surface. Higher magnification is needed to clarify this point.

One particular feature of organic-inorganic hybrids is the possibility of obtaining two products chemically identical as IR spectra of hexyl-modified silica using different solvents show (Figure 2.3), but with different structural properties depending on the experimental conditions. Taking this point into account, different proportions of toluene

Figure 2.2. Left: scanning electron micrograph of methyl-modified silica synthesised using toluene as the solvent. Right: scanning electron micrograph of phenyl-modified silica using toluene as the solvent.
and petroleum ether (100-120°C) were tested (experiments 5-10). Toluene was necessary to dissolve the catalyst and petroleum ether was used to decrease the aggregation of the smallest particles of the hybrid formed.

Figure 2.3. IR spectra of hexyl-modified silica synthesised using various mixtures of petroleum ether (100-120°C) and toluene.

The relative proportions of the two solvents were found to influence the degree of aggregation of the smallest particles; as the solvent is richer in petroleum ether, the aggregation diminishes (Figure 2.4). The best balance of catalyst solubility and reduced aggregation found was a 25:75 volume % mixture of toluene and petroleum ether respectively.
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Figure 2.4. **Left:** scanning electron micrograph of hexyl-modified silica synthesised using 75:25 volume % toluene:petroleum ether as the solvent. **Right:** scanning electron micrograph of hexyl-modified silica using 25:75 volume % toluene:petroleum ether as the solvent.

The level of aggregation observed was reduced in comparison with previous experiments, but it was still too large, so the mixture of solvents chosen was not enough to control the structure of the particles and other strategies were followed.

### 2.3.2 Non-hydrolytic sol-gel synthesis of ormosils using different stirring methods.

Because the non-hydrolytic sol-gel synthesis of these ormosils goes through a 'pseudo-dispersion' polymerisation process, the final properties of the hybrids strongly depend on the degree of phase dispersion. Thus, by increasing the speed of stirring during the process, the size and distribution of the primary particles is expected to change. The nucleation step takes place with the precipitation of these primary particles, and then the precipitation of the hybrid will be around these primary particles. Consequently, a different structure of the ormosils is expected using a different way of stirring.

The polycondensation of different alkyl trichlorosilanes with tetraethyl orthosilicate was carried out using the high speed stirrer (ULTRA TURRAX® dispersion unit) as explained in section 2.2.3.2. Table 2.2 summarises the data of the products obtained.
Chapter 2: Non-hydrolytic sol-gel synthesis of ormosils

| Table 2.2. Results of non-hydrolytic sol-gel synthesis of ormosils using a high speed stirrer. |
|-----------------------------------------------|-------------------------------------------------|-----------------------------------------------|
|    | Financial analysis | IR absorptions (cm$^{-1}$) | Comments and appearance |
|    |                                           | (5580-3300 (v, w), 3290-1650 (w), 1600-1200 (w), 1040-500 (w), 600-540 (w, b)) | Yield and appearance |
|    |                                           |                               | Temp. | Rate. | Solvent | Catalyst | Oxygen donor | Allyl dichlorosilane | Exp. |
|    |                                           |                               |       |       | (toluene + petroleum ether) | PCl$_5$ (0.1 g, 1.3 wt. %) | Si(OEt)$_4$ | (6.00 g, 19 mmol) | (1.89 g, 26 mmol) |   |
| 6 | C, 1.2; H, 3.70; Cl, 3.0 (calcd: C, 1.7; H, 2.71; Cl, 3.0) | 5580-3300 (v, w), 3290-1650 (w), 1600-1200 (w), 1040-500 (w), 600-540 (w, b) | Grey precipitate | 110°C | 3 hours | (4.5 ml + petroleum ether) | PCl$_5$ (0.1 g, 1.3 wt. %) | Si(OEt)$_4$ | (6.00 g, 19 mmol) | (1.89 g, 26 mmol) | 11 |
| 7 | C, 17.4; H, 3.1 (calcd: C, 19.0; H, 3.95) | 3600-3230 (v, w), 2921-2944 (w), 1600-1200 (w), 1040-500 (w), 600-540 (w, b) | Grey precipitate | 110°C | 3 hours | (4.5 ml + petroleum ether) | PCl$_5$ (0.1 g, 1.3 wt. %) | Si(OEt)$_4$ | (6.00 g, 19 mmol) | (1.89 g, 26 mmol) | 12 |
| 8 | C, 3.2; H, 0.8 (calcd: C, 3.95; H, 0.61) | 3590-3300 (v, w), 2957-2967 (w), 1600-1200 (w), 1040-500 (w), 600-540 (w, b) | Grey precipitate | 110°C | 3 hours | (4.5 ml + petroleum ether) | PCl$_5$ (0.1 g, 1.3 wt. %) | Si(OEt)$_4$ | (6.00 g, 19 mmol) | (1.89 g, 26 mmol) | 13 |
| 9 | C, 28.5; H, 3.17; F, 0.8 (calcd: C, 39.5; H, 7.14; F, 0.8) | 3560-3100 (v, w), 2967-2978 (w), 1600-1200 (w), 1040-500 (w), 600-540 (w, b) | Grey precipitate | 110°C | 3 hours | (4.5 ml + petroleum ether) | PCl$_5$ (0.1 g, 1.3 wt. %) | Si(OEt)$_4$ | (6.00 g, 19 mmol) | (1.89 g, 26 mmol) | 14 |

a. Percentages based on weights of MTCS + TEOS.
b. Percentages based on weights of ETCOS + TEOS.
c. Percentages based on weights of HTCS + TEOS.
d. Percentages based on weights of PTCS + TEOS.
e. Yields were calculated based on the theoretical formula of the product.
Lower yields were obtained when using the high speed stirring tool (Ultra Turrax®) (experiments 11-14) than when doing the reaction with a mechanical stirrer. This decrease on the yield could be due to a decrease in the reaction time, leading to an incomplete reaction. This theory could be validated by the elemental analysis: some of the results (experiments 13 and 14) showed less percentage of carbon than was expected (Table 2.2). This could mean that some chains (e.g. hexyl) were cleaved by the high shear forces. The only case where really high yield was obtained was when producing the phenyl-modified silica (exp. no. 14). The IR spectrum of the product (Figure 2.5) shows the presence of some toluene in the obtained solid (absorptions between 3560 and 3300 cm\(^{-1}\) and at 1596 cm\(^{-1}\), which could be due to the toluene or the phenyl group from the phenyl-modified silica).

![Figure 2.5. IR spectrum of phenyl-modified silica synthesised using a mixture of solvents (toluene:petroleum ether 25:75 volume %) and high speed stirrer.](image)

\(^{29}\)Si DP MAS NMR spectra of the products of experiments 11-14 showed a mixture of T (mono-substituted silica) and Q (unmodified silica) species, as it was expected (Figure 2.6). In all the spectra the most intense peaks were T\(^3\) (-64 to -77 ppm) and Q\(^4\) (-106 to -109 ppm) species which means that the predominant silicon species in the samples are RSi(OSi)\(_3\) and Si(OSi)\(_4\) (when doing direct polarisation the relative intensities are quantitative). However, Q\(^3\) species (-104 ppm) were observed as a shoulder of the Q\(^4\) signals in experiments 11-13. This is because there are some oligomers such as
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\[(\text{EtO})\text{Si(OSi)}_3\]\ within the product. \(T^2\) species (-55 ppm) were also found as a shoulder of the \(T^3\) signals, which means that there are oligomers such as \((\text{EtO})\text{RSi(OSi)}_2\).

![Figure 2.6](image)

**Figure 2.6.** \(^{29}\text{Si}\) NMR spectrum of methyl-modified silica synthesised using a mixture of solvents (toluene:petroleum ether 25:75 volume %) and high speed stirrer.

Using the high speed stirrer during the non-hydrolytic sol-gel synthesis of ormosils was found to have the beneficial effect of reducing particle size and aggregation, with the smallest (irregular) particles having diameters of approx. 1 \(\mu\text{m}\) (using mechanical stirrer a size of approx. 2 \(\mu\text{m}\) was achieved, Figure 2.7). Also the number of particles was increased when using the Ultra Turrax\textsuperscript{®} (Figure 2.7).

![Figure 2.7](image)

**Figure 2.7.** Scanning electron micrographs of hexyl-modified silica synthesised using 25:75 volume % toluene:petroleum ether as the solvent using Ultra Turrax\textsuperscript{®} (left) and mechanical stirrer (right).
However, the smallest particles still appear with a high degree of aggregation. This is why the next step of the project was the use of surfactants, to try to stabilise the initial dispersion of the hybrid particles, which would have a strong influence on the final structure of the ormosil.

2.3.3 Non-hydrolytic sol-gel synthesis of ormosils using different surfactants as additives.

One possible way to control the structure of the hybrids during their formation was thought to be the use of surfactants (surface active agents). The surfactants reduce the interfacial energy between the hybrid particles, stabilising the dispersion formed. Thus, surfactants were expected to control the aggregation of the smallest particles, and hence some structural properties of the ormosils.

When choosing the surfactants, some considerations had to be taken into account:

- They must not have water or oxygen that could interfere in the condensation process as the oxygen donor of the system.
- They must be not ionic to not interfere in the process and to be compatible with the system.
- They must be in a different range of polarity, to be able to make a comparison on how the polarity of the surfactant would affect the structure of the hybrid.

The different level of polarity of a surfactant is described by the Hydrophile-Lipophile Balance (HLB) scale, which represents the balance between the hydrophilic and hydrophobic parts of the surfactant molecules and indicates the polarity of the molecules in an arbitrary range of 1-40, with the most commonly used surfactants having a value between 1 and 20. The HLB number increases with increasing hydrophilicity. The determination of the value of HLB is normally made analysing interfacial and bulk properties of surfactants.

Five different surfactants within a homologous series of non-ionic polyoxyethylene ethers with different HLB values (Table 2.3) were selected:
Chapter 2: Non-hydrolytic sol-gel synthesis of ormosils

Table 2.3. Surfactant data from Sigma-Aldrich.

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>Name</th>
<th>Structure</th>
<th>HLB</th>
<th>Molecular weight (g.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Brij® 52</strong></td>
<td>Polyoxylethylene 2-cetyl ether</td>
<td>C₁₆H₃₃(OCH₂CH₂)ₙOH n~2</td>
<td>5.3</td>
<td>330</td>
</tr>
<tr>
<td><strong>Brij® 30</strong></td>
<td>Polyoxylethylene 4-lauryl ether</td>
<td>C₁₂H₂₅(OCH₂CH₂)ₙOH n~4</td>
<td>9.7</td>
<td>362</td>
</tr>
<tr>
<td><strong>Brij® 98</strong></td>
<td>Polyoxylethylene 20-oleyl ether</td>
<td>C₁₈H₃₅(OCH₂CH₂)ₙOH n~20</td>
<td>15.3</td>
<td>1,150</td>
</tr>
<tr>
<td><strong>Brij® 92</strong></td>
<td>Polyoxylethylene 2-oleyl ether</td>
<td>C₁₈H₃₅(OCH₂CH₂)ₙOH n~2</td>
<td>4.9</td>
<td>357</td>
</tr>
<tr>
<td><strong>Igepal® co-210</strong></td>
<td>Polyoxylethylene 2-nonylphenyl ether</td>
<td>4-(C₉H₁₉)C₆H₄(OCH₂CH₂)ₙOH n~2</td>
<td>4.6</td>
<td>308</td>
</tr>
</tbody>
</table>

In this polyoxylethylene ether series, the different polarity is due to the different number of polyoxylethylene groups in the structure. Polarity increases as the number of polyoxylethylene groups (n in Table 2.3) is increased.

Although the surfactants selected contain oxygen, they are not expected to act as oxygen donors in the non-hydrolytic sol-gel condensation because:

1. All of them are primary alcohols, and Corriu reported that this reaction (condensation of silane halides with alcohols) does not work with primary alcohols as the oxygen donor⁷ as they are not able to stabilise the carbocation intermediate.

2. The chosen surfactants have a long alkyl chain, which should offer steric hindrance to the ethers acting as oxygen donors in the reaction.

When the work with surfactants started, the first task was to find out the best HLB value for reducing the aggregation of the hybrid particles formed. The first set of experiments was done using surfactants with very different HLB values (5.3, 9.7 and 15.3) (Table 2.4).
## Table 2.4: Results of NHSG synthesis of ormosils using surfactants with different HLB values.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Alkyl-trichlorosilane</th>
<th>Oxygen donor</th>
<th>Surfactant</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Rese. Time</th>
<th>Temp.</th>
<th>Comments and appearance</th>
<th>Yield</th>
<th>IR absorptions (cm⁻¹) (approximate)</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>HexSiCl₃ (3.62 g, 26 mmol)</td>
<td>Si(OR)₄ (4.00 g, 19 mmol)</td>
<td>Br₆H₅ 52 (HLB = 3.3) (0.48 g, 5 wt. %)²</td>
<td>FeCl₃ (0.1 g, 1 wt. %)³</td>
<td>toluene (4.5 ml) + petroleum ether (13.5 ml)</td>
<td>19 hours</td>
<td>110°C</td>
<td>Light grey precipitate</td>
<td>7.2%</td>
<td>3650-3000 (m, b); 2946 (m, sh); 2920 (s, sp); 2851 (m, sp); 1605 (w, b); 1452 (m, sp); 1348 (m, sp); 1293 (m, sp); 1243 (m, sp); 1182 (s, sh); 1040 (vs, sp); 950 (s, sp); 837 (s, sp); 570 (s, b); 620-580 (m, b)</td>
<td>C, 34.6; H, 6.88% (calcd: C, 39.5; H, 7.14%)</td>
</tr>
<tr>
<td>16</td>
<td>HexSiCl₃ (3.62 g, 26 mmol)</td>
<td>Si(OR)₄ (4.00 g, 19 mmol)</td>
<td>Br₆H₅ 30 (HLB = 9.7) (0.48 g, 5 wt. %)²</td>
<td>FeCl₃ (0.1 g, 1 wt. %)³</td>
<td>toluene (4.5 ml) + petroleum ether (13.5 ml)</td>
<td>20 hours</td>
<td>110°C</td>
<td>Black precipitate</td>
<td>0.63%</td>
<td>3650-3000 (m, b); 2945 (m, sh); 2920 (s, sp); 2851 (m, sp); 1607 (w, b); 1453 (m, sp); 1349 (m, sp); 1290 (m, sp); 1244 (m, sp); 1180 (s, sh); 1043 (vs, sp); 952 (s, sp); 837 (s, sp); 574 (s, b); 65-560 (m, b)</td>
<td>C, 29.1; H, 5.42% (calcd: C, 39.5; H, 7.14%)</td>
</tr>
<tr>
<td>17</td>
<td>HexSiCl₃ (3.62 g, 26 mmol)</td>
<td>Si(OR)₄ (4.00 g, 19 mmol)</td>
<td>Br₆H₅ 98 (HLB = 15.3) (0.48 g, 5 wt. %)²</td>
<td>FeCl₃ (0.1 g, 1 wt. %)³</td>
<td>toluene (4.5 ml) + petroleum ether (13.5 ml)</td>
<td>20 hours</td>
<td>110°C</td>
<td>Black rubbery precipitate</td>
<td>7.4%</td>
<td>3670-3000 (m, b); 2943 (m, sh); 2919 (s, sp); 2859 (m, sp); 1608 (w, b); 1449 (m, sp); 1348 (m, sp); 1294 (m, sp); 1242 (m, sp); 1180 (s, sh); 1048 (vs, sp); 942 (s, sp); 837 (s, sp); 652 (s, b); 624-572 (s, b)</td>
<td>C, 29.5; H, 5.28% (calcd: C, 39.5; H, 7.14%)</td>
</tr>
<tr>
<td>18</td>
<td>MeSiCl₃ (3.89 g, 26 mmol)</td>
<td>Si(OR)₄ (4.00 g, 19 mmol)</td>
<td>Br₆H₅ 52 (HLB = 5.3) (0.40 g, 5 wt. %)²</td>
<td>FeCl₃ (0.1 g, 1.3 wt. %)³</td>
<td>toluene (4.5 ml) + petroleum ether (13.5 ml)</td>
<td>21 hours</td>
<td>110°C</td>
<td>Light grey precipitate</td>
<td>85%</td>
<td>3550-5250 (vw, b); 2960 (w, sp); 2915 (w, sp); 2844 (w, sp); 1600 (vw, b); 1271 (s, sp); 1066 (vs, sp); 954 (s, sh); 826 (s, sp); 800 (s, sp); 708 (s, sp); 693 (m, sp); 641 (m, sp); 60-560 (m, b)</td>
<td>C, 19.8; H, 4.72% (calcd: C, 10.7; H, 2.67%)</td>
</tr>
<tr>
<td>19</td>
<td>MeSiCl₃ (3.89 g, 26 mmol)</td>
<td>Si(OR)₄ (4.00 g, 19 mmol)</td>
<td>Br₆H₅ 39 (HLB = 9.7) (0.40 g, 5 wt. %)²</td>
<td>FeCl₃ (0.1 g, 1.3 wt. %)³</td>
<td>toluene (4.5 ml) + petroleum ether (13.5 ml)</td>
<td>22 hours</td>
<td>110°C</td>
<td>Light grey precipitate</td>
<td>81%</td>
<td>3600-3100 (vw, b); 2960 (w, sp); 2914 (w, sp); 2846 (w, sp); 1600 (vw, b); 1271 (s, sp); 1051 (vs, sp); 945 (s, sh); 828 (s, sp); 797 (s, sp); 772 (s, sp); 696 (m, sp); 620-570 (m, b)</td>
<td>C, 19.3; H, 4.56% (calcd: C, 10.7; H, 2.67%)</td>
</tr>
<tr>
<td>20</td>
<td>MeSiCl₃ (3.89 g, 26 mmol)</td>
<td>Si(OR)₄ (4.00 g, 19 mmol)</td>
<td>Br₆H₅ 98 (HLB = 15.3) (0.40 g, 5 wt. %)²</td>
<td>FeCl₃ (0.1 g, 1.3 wt. %)³</td>
<td>toluene (4.5 ml) + petroleum ether (13.5 ml)</td>
<td>20 hours</td>
<td>110°C</td>
<td>Dark grey precipitate</td>
<td>56%</td>
<td>3600-3050 (vw, b); 2949 (w, sp); 2911 (w, sp); 2846 (w, sp); 1600 (vw, b); 1271 (s, sp); 1012 (vs, sp); 944 (s, sh); 823 (s, sh); 795 (s, sp); 772 (s, sp); 697 (m, sp); 620-570 (m, b)</td>
<td>C, 17.6; H, 4.98% (calcd: C, 10.7; H, 2.67%)</td>
</tr>
</tbody>
</table>

Notes:
- Percentages based on weights of HTCS + TEOS.
- Yields were calculated based on the theoretical formula of the product.

Table 2.4: Results of NHSG synthesis of ormosils using surfactants with different HLB values.
Very low yields were observed for the synthesis of hexyl-modified silicas (Table 2.4, experiments 15-17). One possible reason is the distribution of the material when the hybrid is being formed. A possible micellar structure could be formed with the help of the surfactant present in the medium, with all the inorganic content of the hybrid (Si-O-Si groups) inside and the alkyl groups (hexyl chains) outside of the micelle, but covalently linked to the silicon atoms (Figure 2.8).

![Figure 2.8. Possible micellar structure of a particle during the growing process.](image)

In previous experiments no surfactants were used, so the possibility of having this micellar structure was small. However, when using the surfactants to try to control the structure of hybrid particles, there is a drawback with the formation of these micelles, which could interrupt the growing process of the particles, leading to a really low yield. A rubber material was observed (table 2.4, experiments 15-17) because the hexyl groups have relative chain mobility, giving the material an elastomeric character. This elastomeric nature is presumed to arise from the motion of the hexyl chains when interacting with the alkyl chains of petroleum-ether (one of the co-solvents). There is also plenty of solvent present in the products as can be seen in a typical IR spectrum of hexyl-modified silica synthesised using Brij® 52 as additive (exp. no. 15) (Figure 2.9). Typical bands for the presence of toluene within the product are observed (3650-3000 cm⁻¹ from
C-H stretch vibrations and 1605 cm\(^{-1}\) due to C=C stretch vibrations). The presence of oligomers such as \((\text{EtO})_4\text{Si(OSi)}_n\) \((n<4)\) was confirmed because of the presence of Si-O-Et stretching vibrations at 950 cm\(^{-1}\) (Figure 2.9). As a consequence of the formation of the micellar structure, some surfactant was entrapped within the product forming the micelles, and C-O stretching vibrations from polyoxyethylene structures were observed in the IR spectrum (Figure 2.9).

Figure 2.9. IR spectrum of hexyl-modified silica synthesised using a mixture of solvents (toluene:petroleum ether 25:75 volume %) and Brij\textsuperscript{®} 52 (5 wt. % based on weight of reactants) as additive.

\(^{29}\)Si DP MAS NMR spectrum of the hexyl-modified silica synthesised using Brij\textsuperscript{®} 52 as surfactant (exp. no. 15) showed the expected \(T^3\) (-65.3 ppm) and \(Q^4\) (-108.9 ppm) species (Figure 2.10). However, the presence of \(T^2\) (-57.3 ppm) and \(Q^3\) (-101.8 ppm) species in the product indicated that the condensation did not proceed to completion. In agreement with the IR spectrum, there were present oligomers such as \((\text{EtO})\text{HexSi(OSi)}_2\) \((T^2\) species) and \((\text{EtO})\text{Si(OSi)}_3\) \((Q^3\) species). Thus, the formation of the micellar structures when producing hexyl-modified silicates with surfactants as additives interrupted the condensation process as has been confirmed by elemental analysis, IR spectroscopy and \(^{29}\)Si NMR spectroscopy.
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Figure 2.10. $^{29}\text{Si NMR spectrum of hexyl-modified silica synthesised using a mixture of solvents (toluene:petroleum ether 25:75 volume %) and Brij® 52 (5 wt. % based on weight of reactants) as additive.}"

It was thought that the drying method used (8 hours at 60°C in a vacuum oven) was not long enough to eliminate toluene within the products (Figures 2.1, 2.5 and 2.9). Thus, the next sets of ormosils were dried for 48 hours at 60°C in a vacuum oven. The time was the only variable increased because the temperature had to be relatively low, otherwise the organic content could suffer thermal degradation.

In the case of the methyl-modified hybrids (experiments 18-20), the micellar structure was not formed because the alkyl chains (methyl groups) are not as large as the hexyl-modified silicas; therefore no phase separation between inorganic and organic content was expected to happen. The obtained yields (quite high) support this theory. The really high percentages obtained in the elemental analysis may indicate an incomplete reaction, with some oligomers present in the product. Also the presence of solvent could be the cause of these high percentages (Table 2.4). Bands between 3600-3000 cm$^{-1}$ and at approx. 1600 cm$^{-1}$ indicate the possible presence of toluene.

The least polar surfactant (Brij® 52) appeared to be the most effective in producing more regular shaped primary particles of ca. 1 μm diameter (Figure 2.11), while the other surfactants were effective in reducing the overall level of aggregation, such that
secondary particles of ca. 5 µm diameter and 8-9 µm diameter were obtained in the case of Brij® 30 and Brij® 98 respectively.

Figure 2.11. Scanning electron micrographs of methyl-modified silica synthesised using 25:75 volume % toluene:petroleum ether as the solvent using no surfactant (left) and Brij® 52 (right).

The most effective surfactant (Brij® 52) has a HLB value of 5.3, so the effect of different surfactants with similar polarity on the hybrid structure was investigated. Brij® 92 (HLB= 4.9) and Igepal® co-210 (HLB= 4.6) were used as additives to the non-hydrolytic sol-gel reaction in the next set of experiments (Table 2.5).
<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Alkyl-trichlorosilane</th>
<th>Oxygen donor</th>
<th>Surfactant</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Reaction time</th>
<th>Temp.</th>
<th>Comments and appearance</th>
<th>Yield&lt;sup&gt;a&lt;/sup&gt;</th>
<th>IR absorptions (cm&lt;sup&gt;-1&lt;/sup&gt;) (approximate)</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>HexSiCl&lt;sub&gt;3&lt;/sub&gt; (5.62 g, 26 mmol)</td>
<td>Si(OE)₄ (4.00 g, 19 mmol)</td>
<td>Brij&lt;sup&gt;®&lt;/sup&gt; 92 (HLB= 4.9) (0.48 g, 5 wt %)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>FeCl₃ (0.1 g, 1 wt %)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>toluene (4.5 ml) + petroleum ether (1.35 ml)</td>
<td>20 hours</td>
<td>110°C</td>
<td>Black rubber precipitate</td>
<td>13 %</td>
<td>3600-3050 (vw, b); 2946 (a, sp); 2923 (s, sp); 2855 (s, sp); 1602 (vw, b); 1453 (s, sp); 1180 (s, sh); 1019 (s, sh); 754 (s, sh); 836 (s, sp); 791 (s, sp); 679 (s, sp); 606 (s, b)</td>
<td>C, 32.6; H, 6.01 % (calc.: C, 39.5; H, 7.14 %)</td>
</tr>
<tr>
<td>22</td>
<td>HexSiCl&lt;sub&gt;3&lt;/sub&gt; (5.62 g, 26 mmol)</td>
<td>Si(OE)₄ (4.00 g, 19 mmol)</td>
<td>Igepal&lt;sup&gt;®&lt;/sup&gt; copolymer (HLB= 4.6) (0.48 g, 5 wt %)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>FeCl₃ (0.1 g, 1 wt %)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>toluene (4.5 ml) + petroleum ether (1.35 ml)</td>
<td>21 hours</td>
<td>110°C</td>
<td>Black rubber precipitate</td>
<td>49 %</td>
<td>2952 (m, sp); 2925 (s, sp); 2857 (m, sp); 1509 (m, sp); 1455 (m, sp); 1179 (s, sh); 1007 (vs, sp); 961 (s, sh); 831 (s, sp); 794 (s, sp); 717 (s, sh); 682 (s, sp); 600 (s, b)</td>
<td>C, 44.3; H, 7.94 % (calc.: C, 39.5; H, 7.14 %)</td>
</tr>
<tr>
<td>23</td>
<td>MeSiCl&lt;sub&gt;3&lt;/sub&gt; (3.89 g, 26 mmol)</td>
<td>Si(OE)₄ (4.00 g, 19 mmol)</td>
<td>Brij&lt;sup&gt;®&lt;/sup&gt; 92 (HLB= 4.9) (0.39 g, 5 wt %)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>FeCl₃ (0.1 g, 1.3 wt %)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>toluene (4.5 ml) + petroleum ether (1.35 ml)</td>
<td>22 hours</td>
<td>110°C</td>
<td>Dark precipitate</td>
<td>38 %</td>
<td>2956 (vw, sp); 2918 (w, sp); 2844 (vw, sp); 1271 (s, sp); 1015 (vs, sp); 944 (s, sh); 820 (s, sh); 785 (s, sp); 771 (s, sh); 661 (s, sh); 601 (s, b)</td>
<td>C, 20.2; H, 4.42 % (calc.: C, 10.7; H, 2.67 %)</td>
</tr>
<tr>
<td>24</td>
<td>MeSiCl&lt;sub&gt;3&lt;/sub&gt; (3.89 g, 26 mmol)</td>
<td>Si(OE)₄ (4.00 g, 19 mmol)</td>
<td>Igepal&lt;sup&gt;®&lt;/sup&gt; copolymer (HLB= 4.6) (0.39 g, 5 wt %)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>FeCl₃ (0.1 g, 1.3 wt %)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>toluene (4.5 ml) + petroleum ether (1.35 ml)</td>
<td>21 hours</td>
<td>110°C</td>
<td>Light grey precipitate</td>
<td>121 %</td>
<td>3540-3120 (vw, b); 2954 (w, sp); 2918 (w); 2861 (w); 1597 (w, sp); 1451 (vw, sp); 1270 (a, sp); 1010 (vs, sp); 818 (s, sh); 788 (s, sh); 770 (s, sh); 723 (s, sh); 697 (s, sh); 601 (s, b)</td>
<td>C, 28.9; H, 5.40 % (calc.: C, 10.7; H, 2.67 %)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Yields were calculated based on the theoretical formula of the product.

<sup>b</sup> Percentages based on weights of MTCS + TEOS.

<sup>c</sup> Percentages based on weights of HTCS + TEOS.
During the synthesis of hexyl-modified hybrids, the same kind of micellar structure as before (Figure 2.8) was thought to be formed when using Brij® 92 (similar structure to the surfactants used before), because of the low yield (Table 2.5, 13 %) and low carbon and hydrogen percentages (Table 2.5). Also the rubbery appearance of the final product may indicate the formation of the micellar structure commented on before.

On the other hand, when producing hexyl-modified silica using a surfactant with a different structure (Igepal® co-210), better results in the yield (Table 2.5, 49 %) and elemental analysis (Table 2.5) were obtained. It may be due to the different structure of the surfactant used (Figure 2.12).

\[
\begin{align*}
C_{18}H_{35}(OCH_2CH_2)_nOH & \quad C_9H_{19}-(OCH_2CH_2)_{n}OH \\
& \quad n \sim 2
\end{align*}
\]

**Figure 2.12.** Structure of Brij® 92 and Igepal® co-210 respectively.

The shorter hydrophobic chain and the aryl group may have an effect that reduces the formation of the micellar structures during the growing process of the hexyl hybrid particles, so better results were obtained (Table 2.5).

The content of solvent within the final product was reduced by increasing the drying time from 8 to 48 hours at 60°C in a vacuum oven. The characteristic absorptions of toluene are no longer present in the IR spectrum (Figure 2.13).

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Figure 2.13. IR spectra of hexyl modified silica (toluene:petroleum ether, 25:75 volume %, and Brij® 98, 5 wt. %) dried for 8 hours at 60°C in a vacuum oven (top) and hexyl-modified silica (toluene:petroleum ether, 25:75 volume %, and Igepal® co-210, 5 wt. %) dried for 48 hours at 60°C in a vacuum oven.

A surprisingly low yield was obtained in the synthesis of methyl-modified silica using Brij® 92 as additive (Table 2.5, exp. no. 23) when compared to other previous experiments. It could be due to some parameter that affected the kinetics of the reaction, which is very difficult to control. On the other hand, a very high yield was observed when using Igepal® co-210 (Table 2.5, exp. no. 24), and together with the high percentages observed in elemental analysis, may mean that there is still solvent (Figure 2.14) and/or starting materials present within the product.

Figure 2.14. IR spectrum of methyl-modified silica (toluene/petroleum ether, 25:75 volume %) using Igepal® co-210 as additive (5 wt. %).
The morphology of the hybrids was not very different to those previously synthesised using a surfactant with similar polarity. Particles of ca. 1 μm diameter (Figure 2.15) were observed in the methyl-modified silica when using both Brij® 92 and Igepal® co-210, although using Igepal® co-210 looks to yield fewer particles than using Brij® 92.

Figure 2.15. Scanning electron micrographs of methyl-modified silica synthesised using 25:75 volume % toluene:petroleum ether as the solvent using Brij® 92 (left) and Igepal® co-210 (right) as additive.

2.3.4 Non-hydrolytic sol-gel synthesis of ormosils using Brij® 52 under different conditions.

2.3.4.1 Non-hydrolytic sol-gel synthesis of ormosils with the surfactant added after the reaction.

In an effort to explore the moment during the process when the surfactant is producing the stabilising effect, the surfactant was added to the mixture once the reaction had been finished. The non-hydrolytic route is thought to involve 2 processes: the chemical condensation and the physical process of formation and growth of hybrid particles.

The reactions were carried out as before (section 2.3.3) with the only difference being the addition of surfactant after the reaction was completed (Table 2.6).
### Table 2.6. Results of NHSG synthesis of ormosils with the surfactant added after the reaction.

<table>
<thead>
<tr>
<th>Elemental analysis</th>
<th>IR absorptions (cm(^{-1}))</th>
<th>Yield</th>
<th>Comments and appearance</th>
<th>Surfactant and reaction temp.</th>
<th>React. time</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Oxygen donor</th>
<th>Alcoholtriol-silane</th>
<th>Exp. no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 41.7; H: 2.7; C: 39.5; H: 7.1%</td>
<td>3560-3550, 3200, 2922, 2855, 1456, 1180, 1010, 958, 841, 697, 600</td>
<td>66%</td>
<td>Dark precipitate</td>
<td>Br(\text{II})\text{O} _2 \text{H} \times \text{CH} \text{H}_2 \text{OH} \times \text{CH} \text{H}_2 \text{OH} \times \text{CH} \text{H}_2 \text{OH} \times \text{CH} \text{H}_2 \text{OH} \times</td>
<td>22 hours</td>
<td>toluene + petroleum ether (1:3.5 ml)</td>
<td>FeCl(_3) \text{H} \text{2O}</td>
<td>Si(OEt)(_4) \text{H}</td>
<td>(3.65 g, 25 mmol)</td>
<td>25</td>
</tr>
<tr>
<td>C: 47.2; H: 10.7; C: 20.4%</td>
<td>2960 (s, sp), 2846 (s, sp), 170 (s), 1010 (s, sh), 788 (s, sh), 769 (s, sh), 604 (s, b)</td>
<td>108%</td>
<td>Dark precipitate</td>
<td>Br(\text{II})\text{O} _2 \text{H} \times \text{CH} \text{H}_2 \text{OH} \times \text{CH} \text{H}_2 \text{OH} \times \text{CH} \text{H}_2 \text{OH} \times \text{CH} \text{H}_2 \text{OH} \times</td>
<td>20 hours</td>
<td>toluene + petroleum ether (1:3.5 ml)</td>
<td>FeCl(_3) \text{H} \text{2O}</td>
<td>Si(OEt)(_4) \text{H}</td>
<td>(3.65 g, 25 mmol)</td>
<td>26</td>
</tr>
</tbody>
</table>

a. Percentages based on weights of HTCS + TEOS.

b. Percentages based on weights of MTCS + TEOS.

c. Yields were calculated based on the theoretical formula of the product.
Because the surfactant was added when the reaction was finished, it was not producing the stabilising effect during the chemical process of condensation. In the case of hexyl-modified silica, because the surfactant was not present during the reaction, the formation of micellar structures was not favoured. It may be for this reason that the yield is high (66%, Table 2.6) and the elemental analysis was in quite good agreement with the theoretical value (Table 2.6). The lack of formation of micellar structures during the growing process may lead to the conclusion that hybrid particles are being formed at the same time as the condensation is taking place. Therefore, there are not very clear borders between both chemical and physical processes; possibly the physical process of formation and growing particles may start before the chemical process of condensation finishes. In the case of pure silica (SiO$_2$), the condensation process takes place in such a way as to maximise the number of Si-O-Si bonds, leading to condensed oligomers which are the cores of colloidal particles. Further condensation of monomers with these nuclei leads to the formation of the particles. Thus, the colloidal solution is formed even before all the monomers have been condensed.

When analysing the data from the non-hydrolytic sol-gel synthesis of methyl-modified silica (Table 2.6), the really high yield together with the high percentages of carbon and hydrogen in elemental analysis may arise from the incomplete reaction explained earlier. Some starting and/or intermediate materials may be present within the product. The possibility of having solvent within the dried product was denied according to the IR spectrum of the product (Figure 2.16).
Adding the surfactant once the reaction had been produced did not have an important effect on the morphology of the ormosil particles. The smallest (irregular) particles (ca. 1 μm diameter in the case of methyl modified silica) were in a high degree of aggregation (Figure 2.17, right picture). Because the morphology of the hybrid particles looked the same as when no surfactant was added (Figure 2.17), it could be deduced that the formation of the particles was produced at the same time as the chemical process was taking place, and once the surfactant was added (after 20 hours of reaction), the particles were already formed, so no effect was produced using this variation of the process.
2.3.4.2 Non-hydrolytic sol-gel synthesis of ormosils: dispersing the sol in water.

Another variation to the normal procedure was tested. The colloidal solution was formed during the reaction, and when the reaction finished, the obtained sol was dispersed in water, so the original particles were dispersed in an aqueous medium and a different structure of the hybrid was also expected.

During the dispersion with the Ultra Turrax® stirrer, small droplets of the sol were formed and were observed to float on the water. The obtained yield (34 %) is too low if a comparison is done with other syntheses of methyl-modified silica (between 80 and 100 %, see previous experiments). This drop could be because when dispersing the sol in water some parameter affected the kinetics of the reaction. This theory could be validated by the elemental analysis (C, 18.3; H, 4.16 % [calculated C, 10.6; H, 2.67 %]); maybe the reaction is not completed because of interruption when dispersed, so there are still some oligomers and/or starting materials that can affect the results of the elemental analysis.

Scanning electron microscopy showed the same kind of irregular agglomerations as those observed in previous work. A comparison between the same ormosil (methyl-modified silica) synthesised using the same surfactant (Brij® 52) but without dispersing the system in water is below (Figure 2.18).
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Figure 2.18. Scanning electron micrographs of methyl-modified silica synthesised using 25:75 volume % toluene:petroleum ether as the solvent and Brij® 52 as the surfactant without dispersion (left) and dispersed in water (right).

Smaller primary particles were achieved dispersing the sol in water (less than 1μm diameter), but, on the other hand, the spherical shape found in previous work (Figure 2.18) was lost. The usual irregular agglomeration was obtained with the dispersion in water.

### 2.3.4.3 Non-hydrolytic sol-gel synthesis of ormosils using different amounts of Brij® 52.

The amount of surfactant added to the reaction mixture was increased (10, 20 and 30 wt. %) in an attempt to study how this variation in the concentration of the surfactant was going to affect the final structure of the hybrid. Methyl-modified silica was synthesised under different concentrations of Brij® 52 (Table 2.7).
### Chapter 2: Non-hydrolytic sol-gel synthesis of ormosils

- **a.** Percentages based on weights of MTCS + TEOS.
- **b.** Yields calculated based on the theoretical formula of the products.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Alkyl-trichlorosilane</th>
<th>Oxygen donor</th>
<th>Surfactant</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>React. time</th>
<th>Temp.</th>
<th>Comments and appearance</th>
<th>Yield⁸</th>
<th>IR absorptions (cm⁻¹)</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>Me₅SiCl₃ (3.89 g, 26 mmol)</td>
<td>Si(OE)₃ (4.00 g, 19 mmol)</td>
<td>Brj⁷ 52 (HLB = 5.3) (0.79 g, 10 wt. %)⁻¹</td>
<td>FeCl₃ (0.1 g, 1.3 wt. %)⁻¹</td>
<td>toluene (4.5 ml) + petroleum ether (13.5 ml)</td>
<td>20 hours</td>
<td>110°C</td>
<td>Dark precipitate</td>
<td>99 %</td>
<td>3670-3100 (vw, b); 2962 (w); 2917 (m, sp); 2848 (m, sp); 1271 (s, sp); 1085 (s, sh); 1010 (vs, sp); 816 (s, sh); 788 (s, sh); 768 (s, sp); 718 (s, sh); 626-522 (s, b)</td>
<td>C, 20.4; H, 4.59 % (calc.: C, 10.7; H, 2.67 %)</td>
</tr>
<tr>
<td>29</td>
<td>Me₅SiCl₃ (3.89 g, 26 mmol)</td>
<td>Si(OE)₃ (4.00 g, 19 mmol)</td>
<td>Brj⁷ 52 (HLB = 5.3) (1.58 g, 20 wt. %)⁻¹</td>
<td>FeCl₃ (0.1 g, 1.3 wt. %)⁻¹</td>
<td>toluene (4.5 ml) + petroleum ether (13.5 ml)</td>
<td>20 hours</td>
<td>110°C</td>
<td>Dark precipitate</td>
<td>145 %</td>
<td>2947 (m, sh); 2920 (s, sp); 2851 (s, sp); 1455 (m, sp); 1269 (s, sp); 1094 (s, sh); 1011 (vs, sp); 817 (s, sh); 787 (s, sh); 770 (s, sp); 715 (s, sh); 628-533 (s, b)</td>
<td>C, 52.4; H, 9.62 % (calc.: C, 10.7; H, 2.67 %)</td>
</tr>
<tr>
<td>30</td>
<td>Me₅SiCl₃ (3.89 g, 26 mmol)</td>
<td>Si(OE)₃ (4.00 g, 19 mmol)</td>
<td>Brj⁷ 52 (HLB = 5.3) (2.37 g, 30 wt. %)⁻¹</td>
<td>FeCl₃ (0.1 g, 1.3 wt. %)⁻¹</td>
<td>toluene (4.5 ml) + petroleum ether (13.5 ml)</td>
<td>20 hours</td>
<td>110°C</td>
<td>Dark precipitate</td>
<td>78 %</td>
<td>3570-3030 (w, b); 2946 (m, sh); 2850 (s, sp); 1460 (m, sp); 1270 (s, sp); 1104 (s, sh); 1023 (vs, sp); 941 (s, sh); 826 (s, sh); 785 (s, sh); 770 (s, sp); 718 (s, sp); 630-520 (s, b)</td>
<td>C, 42.1; H, 8.11 % (calc.: C, 10.7; H, 2.67 %)</td>
</tr>
</tbody>
</table>
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The yields obtained during the non-hydrolytic sol-gel synthesis of methyl-modified silica using different concentrations of surfactants were quite high, especially when adding 20% of Brij® 52 (Table 2.7). Also the percentages obtained in the elemental analysis were very high (Table 2.7) and this could be due to the presence of surfactant entrapped in the final product. This theory could be validated by the IR spectra of the products (Figure 2.19). The absorbance intensity of the C-H stretching absorptions increases when increasing the amount of polyoxyethylene 2-cetyl ether (Brij® 52), so the surfactant may be present within the product.

![Figure 2.19](image)

**Figure 2.19.** IR spectra of methyl-modified silica synthesised using different concentrations of Brij® 52.

Very small particles (less than 1 μm in diameter) were observed in the SEM, but the effect of reducing the aggregation of these irregular particles was minimal (Figure 2.20).
2.3.4.4 Non-hydrolytic sol-gel synthesis of ormosils using Brij® 52 without filtering the resulting gel.

During the non-hydrolytic sol-gel synthesis of ormosils, some of the obtained particles were really small (less than 1μm in diameter). One of the concerns was that during the work up process, when filtering the product, those small particles could pass through the filter, losing them. In this set of experiments, the obtained gel was left to dwell in a desiccator with P₂O₅ for 2 days at room temperature. The experiments carried out are summarised in Table 2.8.
Chapter 2: Non-hydrolytic sol-gel synthesis of ormosils

Table 2.8. Results of NHSG synthesis of ormosils using Brij® 52 without filtering the gel obtained.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Elemental analysis</th>
<th>IR absorptions (cm⁻¹)</th>
<th>Comments and appearance</th>
<th>Temp.</th>
<th>React. time</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Surfactant</th>
<th>Oxygen donor</th>
<th>Alkyl-trichlorosilane</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>C, 34.9; H, 7.04%</td>
<td>2945 (m, sp); 2919 (s, sp); 2851 (m, sp); 1453 (w); 1270 (s, sp); 1087 (s, sh); 1013 (vs, sp); 936 (s, sh); 815 (s, sh); 791 (s, sh); 768 (s, sp); 720 (s, sh); 595 (s, b)</td>
<td>Grey precipitate</td>
<td>110°C</td>
<td>20 hours</td>
<td>toluene + petroleum ether (3.5 ml)</td>
<td>Brij® 52 (HLB = 5.3)</td>
<td>0.40 g, 5 wt%</td>
<td>Si(OH)₃ (4.00 g, 19 mmol)</td>
<td>MeSiCl₃ (3.89 g, 26 mmol)</td>
</tr>
<tr>
<td>32</td>
<td>C, 41.5; H, 8.10%</td>
<td>2953 (m, sp); 2920 (s, sp); 2878 (m, sp); 2850 (m, sp); 1458 (m, sp); 1250 (s, sp); 1026 (vs, sp); 997 (vs, sh); 777 (s, sp); 732 (s, sp); 705 (s, sh); 600 (s, b)</td>
<td>Grey precipitate</td>
<td>110°C</td>
<td>20 hours</td>
<td>toluene + petroleum ether (3.5 ml)</td>
<td>Brij® 52 (HLB = 5.3)</td>
<td>0.41 g, 5 wt%</td>
<td>Si(OH)₃ (4.00 g, 19 mmol)</td>
<td>EtSiCl₃ (4.25 g, 26 mmol)</td>
</tr>
<tr>
<td>33</td>
<td>C, 46.0; H, 5.08%</td>
<td>2944 (m, sh); 2920 (s, sp); 2851 (m, sp); 1594 (m, sp); 1431 (s, sp); 1130 (s, sh); 1018 (vs, sh); 997 (vs, sh); 777 (s, sp); 732 (s, sp); 705 (s, sh); 600 (s, b)</td>
<td>Grey precipitate</td>
<td>110°C</td>
<td>20 hours</td>
<td>toluene + petroleum ether (3.5 ml)</td>
<td>Brij® 52 (HLB = 5.3)</td>
<td>0.48 g, 5 wt%</td>
<td>Si(OH)₃ (4.00 g, 19 mmol)</td>
<td>PtSiCl₃ (5.50 g, 26 mmol)</td>
</tr>
</tbody>
</table>

a. Percentages based on weights of MTCS + TEOS.
b. Percentages based on weights of ETCS + TEOS.
c. Percentages based on weights of PTCS + TEOS.
d. Yields calculated based on the theoretical formula of the products.
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Very high yields and elemental analysis data were obtained in all the cases (Table 2.8). One possible reason could be the presence of some by-product entrapped within the product. Ethyl chloride is gaseous under ambient temperature and it is assumed to be removed by the nitrogen flow during the reaction, but some of it could be trapped in the network when being formed. Because there is no washing process after the reaction (filtering was avoided during this set of experiments), some by-product may stay in the obtained product.

Another possible reason for the high yields obtained could be incomplete reaction of the starting materials. As a result some oligomers may be present in the final product, as can be seen in the $^{29}$Si NMR spectrum (Figure 2.21). This fact could be validated with the high percentages obtained in the elemental analysis, due to the possible presence of other materials apart from the ormosil in the final product.

$^{29}$Si CP MAS NMR spectra of these ormosils showed the presence of $T_3$ (-77 ppm), $T_2$ (-64 to -68 ppm), $T_1$ (-56 ppm), $Q_4$ (-110 to -104 ppm) and $Q_3$ (-100 ppm) species. The presence of $T_2$, $T_1$ and $Q_3$ species revealed that the condensation reactions did not go to completion, leaving oligomers within the product such as (EtO)RSi(OSi)$_2$, (EtO)$_2$RSi(OSi) (R= Me, Et or Ph) and (EtO)Si(OSi)$_3$. In the case of phenyl-modified silicate (exp. no. 33), a typical $^{29}$Si NMR spectrum shows the presence of $T_2$, $T_3$, $Q_3$ and $Q_4$ species (Figure 2.21). Because the spectrum was done with cross-polarisation, the relative intensities are not reasonably quantitative.

![Figure 2.21. $^{29}$Si NMR spectrum of phenyl-modified silica synthesised using 25:75 volume % toluene:petroleum ether as the solvent and Brij® S2 as the surfactant without filtering the resulting gel.](image-url)
Spherical particles (Figure 2.22) were obtained when synthesising methyl-modified silicate using the non-hydrolytic sol-gel route without filtering the obtained product. The size distribution of these spherical particles was quite broad, from ca. 100-200 nm to 1-2 μm in diameter. The aggregation degree of these spherical particles was not improved using this new method, as can be seen in the pictures (Figure 2.22).

The non-hydrolytic sol-gel route to ethyl-modified silica produced some interesting particles (Figure 2.23), really small in size (ca. 150 nm diameter), with round shape (but...
not spherical as in the case of methyl-modified silicate) and even more aggregated than in the case of the methyl-modified silicate.

Figure 2.23. Scanning electron micrographs of ethyl-modified silica synthesised using 25:75 volume % toluene:petroleum ether as the solvent and Brij® 52 as the surfactant without filtering the resulting gel.

However, in the case of the synthesis of phenyl-modified silicate under the same conditions, very irregular and aggregated particles were found.

In previous experiments, the gel products were washed with ether and filtered. It is possible that during this filtration (under vacuum), the physical stress produced could lead to a coalescence of the particles previously formed; the subsequence drying of the product would also produce shrinkage within the structure of the product, leading to particles with irregular shapes and sizes. On the other hand, when the obtained gel was left to dwell in a desiccator with P₂O₅ for two days, the particles formed during the sol-gel process are not under any major physical stress as they were in previous experiments. Therefore, the obtained particles in the final products would keep the shape that they had when they were produced. This could be a possible reason of obtaining spherical particles when changing the work up of the reaction.

These last 3 experiments (experiments 31-33) showed the importance of the organic group in the final structure of the hybrid. The smaller the alkyl group (methyl group), the
more spherical the particles. When the organic content is larger, as in the case of ethyl groups, the particles are not spherical anymore, but they still have a rounded structure. When using phenyl groups as the organic content of the hybrid, irregular and larger particles were produced.

2.3.5 Non-hydrolytic sol-gel synthesis of silicon dioxide under typical conditions.

The non-hydrolytic sol-gel synthesis of silicon dioxide was carried out in order to use the product as a reference for the ormosils previously synthesised. A quite good yield was obtained (90 %) and the product was solvent-free, since no IR absorptions for the solvents were observed (Figure 2.24). The network formed by the Si-O bonds was confirmed by IR spectroscopy (figure 2.24). However, the condensation did not go to completion because of the presence of Si-O-Et stretching absorptions at ca. 930 cm\(^{-1}\). Thus, there are oligomers such as \((\text{EtO})_{4-n}\text{Si(OSi)}_n\).

![Figure 2.24. IR spectrum of silicon dioxide synthesised via the non-hydrolytic sol-gel route using a mixture of toluene:petroleum ether (25:75 volume %) as the solvent and FeCl\(_3\) (1.1 wt %) as the catalyst.](image)

Large aggregated, irregular particles of diameter \(ca. 5 \, \mu m\) were obtained when analysing the silicon dioxide structure.
2.3.6 Non-hydrolytic sol-gel synthesis of ormosils using polystyrene as an additive.

Viscosity has been investigated as a possible parameter to control the size and morphology of metal particles\(^9\) (it permits the control of the aggregation step of the growth mechanism); a possible way to increase the viscosity of the reacting medium is the use of polystyrene as an additive. Polystyrene polymers added to a colloidal suspension may control the group-wise behaviour of the colloidal particles.

Different amounts of different polystyrenes (different molecular weight) were tested (Table 2.9).
Table 2.9. Results of NHSG synthesis of ormosils using polystyrene as an additive.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Percentages based on weights of HTCS + TEOS.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a. Yields calculated based on the theoretical formula of the product.</td>
</tr>
<tr>
<td></td>
<td>b. Percentages based on weights of MTCS + TEOS.</td>
</tr>
<tr>
<td></td>
<td>c. Yields calculated based on the theoretical formula of the product.</td>
</tr>
<tr>
<td></td>
<td>d. Percentages based on weights of toluene (d. 0.865 g.cc⁻¹) + petroleum ether (d. 0.640 g.cc⁻¹).</td>
</tr>
</tbody>
</table>
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After the reaction, all the materials were filtered and washed with ether, so the polystyrene was separated from the products (no IR typical absorptions of polystyrene were observed, Table 2.9). They were all dried in a vacuum oven at 60°C for 48 hours, and grey precipitates were obtained in all cases.

Quite high yields were obtained (Table 2.9), and in the majority of the cases, really high values were obtained for elemental analysis, leading to the possibility of having some unreacted starting materials and/or oligomers within the product.

The morphology of the obtained products was not very different from previous results. Irregular, aggregated hybrid particles were obtained with a size ranging from 0.5 μm to 5 μm. However, when increasing the viscosity significantly using 20 % (percentage based on weight of the solvent used) of polystyrene ($M_n$ ca. 45,000) (exp. no. 41), spherical shapes were found on some of the primary particles (Figure 2.25).

![Figure 2.25. Scanning electron micrographs of methyl-modified silica using 20 % (based on weight of solvent) of polystyrene ($M_n$ ca. 45,000) during the non-hydrolytic sol-gel synthesis.](image)

The final structure of the particles is strongly influenced by the colloidal state of the product during the process. The polymer colloid is formed by dispersion of a polymer in a solvent. The movement of the small particles in the dispersion medium is governed by the Brownian motion, which makes to the particles to be in constant motion and colliding with each other$^{10}$. The viscosity of the medium has a strong influence in the movement of
the particles, and the Brownian motion of a single particle in a liquid medium can be related to the viscosity by the Stokes-Einstein equation,

\[ D_c = \frac{k_B T}{6\pi \eta a_0} \] (2.5)

where \( D_c \) is the Brownian diffusion coefficient, \( k_B \) is Boltzmann's constant, \( T \) is the absolute temperature, \( \eta \) is the viscosity of the fluid and \( a_0 \) is the radius of the particle.

Thus, attending to the Stokes-Einstein equation (Equation 2.5), for the same kind of material (same radius of the particle), at the same temperature, an increase in the viscosity of the medium (using polystyrene) leads to a decrease in the Brownian motion of the particles. Therefore, there is less probability of coalescence of the particles since the movement is limited, and the aggregation of these particles is lower.

### 2.3.7 Non-hydrolytic sol-gel synthesis of silsesquioxanes using DMSO as the oxygen donor.

It was thought that using DMSO as an oxygen donor in the non-hydrolytic sol-gel condensation, an easy reaction could take place with alkyl chlorosilanes, since DMSO is known to be a good silaphilic nucleophile. DMSO was already investigated in the past as an oxygen donor to certain metal halides (boron, silicon or tin halides), yielding different complexes.

A disadvantage of using the non-hydrolytic sol-gel route with TEOS as oxygen donor is the need for a catalyst (FeCl₃) for the condensation reaction to happen. This Lewis acid can contaminate the final product and also produce discoloration of the otherwise colourless ormosil. The reaction with DMSO as oxygen donor would work without the use of a catalyst and therefore iron(III) chloride would not be present in the final product, leading to a white powder which could be useful for future applications; DMSO itself would act as the solvent for the reaction (Equation 2.3).

\[ 2RSiCl_3 + 30S(CH_3)_2 \rightarrow R_2Si_2O_3 + 3CH_3SCH_2Cl + 3HCl \] (2.3)
DMSO is known to be one of a group of silaphilic molecules that can activate silicon to nucleophilic attack via pentacoordinate intermediates. The initial reaction of DMSO with a silicon halide has been previously described in the literature (Figure 2.26).

![Figure 2.26. Initial reaction of a silicon halide with DMSO.](image)

From this scheme (Figure 2.26), the expected reaction mechanism of alkyl-trichlorosilane was deduced as follows (Figure 2.27):

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Figure 2.27. Reaction mechanism of the condensation between DMSO and alkyl chlorosilane to yield a silsesquioxane.

The reaction starts with the donation of 2 electrons from the S=O π bond to the silicon centre of the silicon chloride, forming a pentacoordinate state (Figure 2.27). A Pummerer rearrangement follows producing a cleavage of the sulfur oxygen bond, and yielding an oxosilicon intermediate that attacks a new molecule of alkyl trichlorosilane and forms a silicon oxobridge (Si-O-Si structure) with an alkyl group covalently attached to every silicon atom (these kinds of ormosils are called silsesquioxanes). The whole process is repeated several times leading to the formation of a three-dimensional network of Si-O-Si structures \((R_2Si_2O_3)_n\). Formation of HCl (see Equation 2.3) accompanied the exothermic reaction.

Table 2.10 summarises the experiments carried out.
### Table 2.10. Results of NHSG synthesis of silsesquioxanes using DMSO as the oxygen donor.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Alkyl-trichlorosilane</th>
<th>Oxygen donor</th>
<th>React. time</th>
<th>Product</th>
<th>Yield</th>
<th>Physical appearance</th>
<th>IR absorptions (cm⁻¹) (approximate)</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>MeSiCl₃ (3.89 g, 26 mmol)</td>
<td>DMSO (25 ml)</td>
<td>2 hours</td>
<td>(Me₂Si₂O₃)ₙ</td>
<td>80 %</td>
<td>Light white powder</td>
<td>2972 (w, sp); 1409 (vw); 1271 (s, sp); 1041 (vs, sh); 988 (vs, sp); 857 (s, sp); 762 (vs, sp); 669 (s, b); 605-540 (s, b)</td>
<td>C, 14.9; H, 4.83 % (calc.: C, 17.9; H, 4.48 %)</td>
</tr>
<tr>
<td>43</td>
<td>EtSiCl₃ (4.25 g, 26 mmol)</td>
<td>DMSO (25 ml)</td>
<td>2 hours</td>
<td>(Et₂Si₂O₃)ₙ</td>
<td>98 %</td>
<td>Light white powder</td>
<td>2960 (m, sp); 2930 (w); 2911 (w); 2879 (m, sp); 1460 (m, sp); 1414 (w, sp); 1252 (s, sp); 1050 (s, sh); 985 (vs, sp); 959 (vs, sh); 756 (s, b); 691 (s, sp); 625-570 (m, b)</td>
<td>C, 22.3; H, 6.42 % (calc.: C, 29.6; H, 6.17 %)</td>
</tr>
<tr>
<td>44</td>
<td>HexSiCl₃ (5.62 g, 26 mmol)</td>
<td>DMSO (25 ml)</td>
<td>2 hours</td>
<td>(Hex₂Si₂O₃)ₙ</td>
<td>30 %</td>
<td>White rubbery product</td>
<td>2957 (s, sp); 2924 (s, sp); 2858 (s, sp); 1467 (m, sp); 1407 (w, sp); 1378 (w, sp); 1192 (s, sp); 1087 (s, sh); 1055 (s, sp); 986 (vs, sp); 797 (s, sp); 687 (s, sp)</td>
<td>C, 50.8; H, 9.97 % (calc.: C, 52.5; H, 9.49 %)</td>
</tr>
<tr>
<td>45</td>
<td>PhSiCl₃ (5.50 g, 26 mmol)</td>
<td>DMSO (25 ml)</td>
<td>2 hours</td>
<td>(Ph₂Si₂O₃)ₙ</td>
<td>79 %</td>
<td>Light white powder</td>
<td>3063 (vw); 3050 (vw); 1694 (w); 1595 (m, sp); 1430 (s, sp); 1131 (s, sp); 1052 (s, sp); 1027 (s, sh); 987 (vs, sp); 922 (s, sh); 848 (s, sh); 778 (s, sp); 750 (s, sp); 693 (vs, sp); 649 (s, sh)</td>
<td>C, 53.5; H, 3.95 % (calc.: C, 55.8; H, 3.88 %)</td>
</tr>
</tbody>
</table>

a. Yields calculated based on the theoretical formula of the product.
All yields were quite high, except for the case of the hexyl-modified product. As previously stated it is thought that the long hexyl chains form a possible micellar structure with all the inorganic material (Si-O-Si groups) outside and the alkyl groups inside. Because DMSO is highly polar, the material of the hybrid is reorientated, leading to the inverse situation discussed in section 2.3.3, where the inorganic material was inside the micellar structure and the long hexyl chains were outside interacting with the solvent (mixture of toluene and petroleum ether).

The formation of this structure could interrupt the condensation process between all the oligomers, and then subsequently the growing process, so quite low yields are achieved in comparison with other silsesquioxanes. During the work up of this reaction (exp. no. 44), instead of having a solid powder as in other silsesquioxanes (experiments 42, 43 and 45), a white rubbery product was obtained.

$^{29}\text{Si} \text{ DP MAS NMR}$ spectrum of hexyl-silsesquioxane (Figure 2.28) revealed the formation of siloxane bonds with characteristic resonances for $T^1$ (-54.5 ppm), $T^2$ (-58.1 ppm) and $T^3$ (-65.9 ppm) species. The condensation process did not go to completion because of the presence of $T^1$ and $T^2$ species (oligomers such as $(\text{EtO})_2\text{HexSi(OSi)}$ and $(\text{EtO})\text{HexSi(OSi)}_2$ respectively), in agreement with the yield obtained for the hexyl-silsesquioxane experiment (exp. no. 44). No Q species were observed in the spectrum, which means that no Si-C bonds were broken as a result of the non-hydrolytic process. Because the spectrum was done with direct-polarisation, the relative intensities are quantitative ($T^3= 39.4\ %$, $T^2= 29.8\ %$ and $T^1= 24.2\ %$).
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**Figure 2.28.** $^{29}$Si NMR spectrum of $(\text{Hex}_2\text{Si}_2\text{O}_3)_n$ synthesised via the non-hydrolytic sol-gel route using DMSO as an oxygen donor.

$^{29}$Si DP MAS NMR spectra of the other silsesquioxanes (experiments 42, 43 and 45) showed the same tendency of no completion of the condensation process, because there were present T$_1$ (-53 to -67 ppm) and T$_2$ (-57 to -71 ppm) species (oligomers), apart from T$_3$ (-64 to -77 ppm) species (fully condensed silicon centres).

Elemental analyses gave a reasonable correlation with the theoretical values but not in the case of the ethyl-modified product (exp. no. 43), where a gap of 8% in the amount of carbon present between experimental and calculated values, showing a decrease in the organic content in the hybrid.

DMSO was also used as the reaction solvent, so the hybrid network is formed under a different polar environment than when using the mixture of toluene and petroleum ether (previous synthesis of ormosils, experiments 5-41). As a consequence of that, changes in the morphology of the ormosils were expected; the more polar medium is forcing a reorientation of the organic component within the hybrid. This new morphology was studied using SEM (Figure 2.29).
Spherical particles were observed in the methyl-modified silsesquioxane structure (Figure 2.29), with a diameter of ca. 1 μm. The change in the reaction medium has influenced the structure of the hybrid particles.

The organic content of the ormosil has also been shown to play an important role in the final structure of the hybrid. When larger alkyl chains are forming the hybrid, such as ethyl or hexyl chains, the spherical shape of the primary particles is lost (Figure 2.30), and also the size of them is larger than that observed for methyl-silsesquioxane (5-10 μm in diameter). This tendency was also observed in the case of phenyl-silsesquioxane (Figure 2.30).
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2.3.8 Non-hydrolytic sol-gel synthesis of silicon dioxide using DMSO as the oxygen donor.

Silicon dioxide was synthesised (Equation 2.4) under the same conditions as in the case of silsesquioxanes. Thus, comparisons can be made between silsesquioxanes (organic-inorganic hybrid) and SiO₂ (only inorganic content).

\[
\text{SiCl}_4 + 2\text{OS(CH}_3)_2 \rightarrow \text{SiO}_2 + 2\text{CH}_3\text{SCH}_2\text{Cl} + 2\text{HCl}
\]  

(2.4)

This reaction was done in the past\textsuperscript{12} using different conditions: stoichiometry 1:1 (DMSO:SiCl₄) using dichloromethane as the solvent at 0°C.

In the elemental analysis of the product it was found a high content of carbon (6.14 %) and hydrogen (1.95 %), so some solvent contamination (DMSO) was present in the final product. This thesis was corroborated by analysing the IR spectrum of the product (Figure 2.31). Typical DMSO-water absorption could be observed at 1680 cm\textsuperscript{-1} (S=O-OH group), which could be due to the presence of solvent + washing agent (H₂O) in the product. The characteristic broad absorption of water was observed at 3500-3000 cm\textsuperscript{-1}. It is also possible that the condensation reaction did not go to completion, because of the presence of Si-O-H stretching vibrations at \textit{ca.} 940 cm\textsuperscript{-1} (Figure 2.31), which reveals the possible presence of oligomers within the product.
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Figure 2.31. IR spectrum of \((\text{SiO}_2)_n\) synthesised via the non-hydrolytic sol-gel route using DMSO as an oxygen donor.

\(^{29}\text{Si}\) DP MAS NMR spectrum (Figure 2.32) revealed the presence of \(Q^4\) (-110 ppm), \(Q^3\) (-100.9 ppm) and \(Q^2\) (-91.2 ppm) species. The absence of \(Q^0\) species means that although the condensation did not proceed to completion (presence of groups \(Q^3\) and \(Q^2\)), no monomer was left unreacted. Thus, oligomers such as \((\text{HO})_2\text{Si(OSi)}_2\) and \((\text{HO})\text{Si(OSi)}_3\) (\(Q^2\) and \(Q^3\) respectively) were found within the product, as has been mentioned before attending to elemental analysis and IR spectrum of the product. Because the spectrum was done with direct-polarisation, the relative intensities are quantitative (\(Q^4=58.6\%\), \(Q^3=36.5\%\) and \(Q^2=4.90\%\)).

Figure 2.32. \(^{29}\text{Si}\) NMR spectrum of \((\text{SiO}_2)_n\) synthesised via the non-hydrolytic sol-gel route using DMSO as an oxygen donor.
Significantly different structures were observed in silicon dioxide compared to those found for the previous silsesquioxanes (Figure 2.33). Very irregular particles (in a range of 1-25 μm in diameter) were found. This could be due to the key role the alkyl chain plays during the formation of the hybrid network. A big difference is observed when there is no organic content present during the synthesis of the network (Figure 2.33).

![Figure 2.33. Scanning electron micrographs of (Me₂Si₂O₃)ₙ (left) and (SiO₂)ₙ (right) synthesised via the non-hydrolytic sol-gel route using DMSO as an oxygen donor.](image)

### 2.4 Conclusions.

A variety of sol-gel synthetic routes have been studied in an effort to produce organic-inorganic hybrid (nano)particles. Use of a non-hydrolytic sol-gel route successfully produces hybrid ormosils, whose morphology can be varied depending on the nature of the solvent; the type of stirring; the presence, type and concentration of surfactant; and the presence and concentration of polystyrene as additive during the synthesis.

Four different organic groups (methyl, ethyl, hexyl and phenyl) were introduced into the hybrid to evaluate how the organic content affects the morphology of the resulting ormosil. The size of the organic moiety was found to be an important factor in the structure of the hybrid, because under certain conditions (using Brij® 52 as surfactant or using DMSO as oxygen donor) spherical particles were obtained using methyl substituents, while under the same conditions, the ethyl-modified silicate particles were found with irregular shapes.
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The first part of the work was based on the optimisation of the ‘pseudo dispersion polymerisation’ conditions in order to try to produce controlled particles. Different parameters were tested:

- **Solvent**: an appropriate solvent is necessary to dissolve the catalyst (solid) and homogenise the precursors. A mixture of toluene and petroleum ether (100-120°C) (25:75 volume %) was found to be the most effective in reducing the aggregation of the smallest particles.

- **Stirring methods**: an overhead mechanical stirrer was used early in the work, but the level of stirring was increased using a high speed stirrer (Ultra Turrax®), achieving a decrease in the particle size.

- **Different surfactants** were used to control the aggregation of the smallest particles. A range of five non-ionic polyoxyethylene ethers with different polarities was used, and the least polar of them (Brij® 52) was found to be the most effective, achieving spherical particles in the size range 100 nm-1 μm (Figure 2.22).

- **Different amounts of polystyrene** were added to increase the viscosity of the colloidal solution, interfering with the aggregation of the smallest particles. Highly viscous solutions (20 % of polystyrene [Mₙ ca. 45,000] based on the amount of solvent) were found to be partially successful (spherical particles with relative low aggregation).

- **Oxygen donor**: DMSO was used as the oxygen donor for the process, acting also as the solvent. The change in the polarity of the medium affected the growing process of the ormosil, producing spherical silsesquioxane particles of ca. 1μm diameter (Figure 2.29).

For the first time, some control over the product morphology during the non-hydrolytic sol-gel (NHSG) synthesis of ormosils has been achieved. In the past, ormosils have been synthesised in a NHSG solvent-free route, but no control over the morphology of the particles was achieved\(^4,5\). In the present work, the use of solvents in which the precursors are soluble, lead to ormosil spherical particles, where the inorganic content (silica) of the
hybrid is forming the core of the particles and the organic groups project into the non-polar solvent surrounding the inorganic oxide.
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2.5 References.

Chapter 3

Use of ormosils as additives to epoxy resins
Chapter 3: Use of ormosils as additives to epoxy resins

3.1 Introduction.

An epoxy resin is defined as a molecule containing more than one oxirane group. This three-membered ring (Figure 3.1) is also known as the epoxy, epoxide, or ethoxyline group\(^1\). Such molecules are polymerised through the epoxide groups using a crosslinking agent (also called hardener or curing agent) to form a three-dimensional network.

![Figure 3.1. Structure of oxirane group.](image)

Different commercial epoxy resins have been developed with aliphatic, cycloaliphatic or aromatic backbones. They are versatile materials because of the possibility of the epoxy rings reacting with a variety of substrates.

Epoxy resins are now used in a wide variety of industries because of their polyvalent properties. Some important characteristics of these epoxy resins are: high chemical and corrosion resistance, good mechanical and thermal properties, outstanding adhesion to various substrates, low shrinkage upon cure, flexibility, good electrical properties, and ability to be processed under a variety of conditions\(^1\).

3.1.1 Historical review.

Two different research groups initially worked with epoxy resins: DeTrey Frères (Switzerland) and DeVoe and Raynolds (USA). In 1936, the European side (Castan, a Swiss chemist working for DeTrey Frères) was investigating a low melting bisphenol-A-based epoxy resin that gave a thermoset composition when cured with phthalic anhydride for dental products\(^2\). At the same time, the American paint company DeVoe and Raynolds was working with epoxy resins for use in the coatings industry. They were also working with epichlorohydrin-bisphenol-A systems (Figure 3.2), and combining them with other materials (phenolic or amino resins) to form surface coatings\(^2\).

![Figure 3.2. Structure of epichlorohydrin-bisphenol-A resin systems\(^2\).](image)
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The largest development of these epoxy resins came with the licensing agreement between both companies and the suppliers of bisphenol-A (Bakelite) and epichlorohydrin (Shell) in 1955. Since then, a large number of different epoxy resins have been patented with very different possible applications.\(^1\)

In the 1960s glycidylated o-cresol novolac resins (Figure 3.3) were developed by CIBA Products Co. for use as high temperature-resistant polymers. The Dow Chemical Co. introduced glycidylated phenol novolac resins (Figure 3.3) and Shell manufactured polyglycidyl ethers of tetrafunctional phenols.\(^1\)

![Figure 3.3. Structure of novolac resins.](image)

**3.1.2 Synthesis of epoxy resins.**

The synthesis of epoxy resins is based on the reaction of compounds containing an active hydrogen group with epichlorohydrin followed by dehydrohalogenation (Figure 3.4)\(^1\):

$$X-H + CH_2=CH CH_2-Cl \rightarrow X-CH_2=CH CH_2-Cl \xrightarrow{HCl} X-CH_2-CH CH_2$$

\(X= R-O, R-NH-\)

*Figure 3.4. Synthesis of epoxy resins from epichlorohydrin.*

Another method involves the direct epoxidation of olefins by peracids (Figure 3.5):

$$R-CH=CH R' + R'' COOH \rightarrow R-CH=CH R' + R'' COOH$$

*Figure 3.5. Synthesis of epoxy resins from olefins.***
The most widely used epoxy resin is the product of the reaction of excess epichlorohydrin and bisphenol-A to yield the liquid resin diglycidyl ether of bisphenol-A (DGEBA) (Figure 3.6):

![Reaction scheme for the synthesis of DGEBA](image)

Figure 3.6. Synthesis of liquid epichlorohydrin-bisphenol-A resins.

The reactivity of epoxy resins is characterised by the reactive oxirane ring which can be reacted with curing agents (during the curing process) or homopolymerised to form a crosslinked polymeric structure. The former is the most important process in epoxy resin technology and is detailed below.

### 3.1.3 Curing process.

As mentioned above, the curing process is the most important process in epoxy resin technology. It consists of the conversion of the resin into a hard, infusible three-dimensional network where the resin molecules are crosslinked together by means of strong covalent bonds. Their conversion from liquids or meltable solids to cured thermosets by chemical hardeners and catalysts gives them an extremely versatile utility. The final properties of an epoxy resin largely depend on the curing system used to convert it into a crosslinked network.

The curing reaction is exothermic, thus heat is produced during the crosslinking process. An increase in the temperature of the system is produced, and special care has to be taken if large amounts of epoxy resin and hardener are being mixed together.

### 3.1.3.1 Curing agents.

As mentioned above, a three-dimensional insoluble and infusible network is formed when the resin is treated with a curing agent or hardener. The selection of the hardener depends
on processing methods, curing conditions and the physical and chemical properties required from the final product. The hardener, indeed, can be either catalytic or co-reactive:

- **Catalytic curing agent**: this works as an initiator for epoxy resin homopolymerisation (the resin reacts with itself) (Figure 3.7). These are normally used at less than 10 parts per hundred of resin (phr).

![Figure 3.7. Reaction of an epoxy resin with a catalytic curing agent.](image)

- **Co-reactive curing agent**: it functions as a co-monomer in the polymerisation process. The used hardener (nadic methyl anhydride) reacts as a co-monomer with the selected epoxy resin (triglycidyl-\(p\)-aminophenol) (Figure 3.8):

![Figure 3.8. Scheme of reaction of triglycidyl-\(p\)-aminophenol with nadic methyl anhydride.](image)

The hardener enters into the crosslinking reaction (Figure 3.8 represents one of the branches of the trifunctional epoxy resin used during this work). The exact amount
required will depend on the chemical balance of reactive sites on the hardener molecule compared to the reactive sites of the resin.

One of the most used groups of curing agents is acid anhydrides. The most important ones are those based on a cycloaliphatic structure (Figure 3.9).2

Figure 3.9. Structure of the anhydride hardeners most used in the past. (a) Phthalic anhydride (PA); (b) tetrahydrophthalic anhydride (THPA); (c) hexahydrophthalic anhydride (HHPA); (d) nadic methyl anhydride (NMA); (e) chlorendic anhydride; (f) pyromellitic dianhydride (PMDA).2

Nadic methyl anhydride (NMA) has been widely used for electrical laminating and filament winding applications. Its mixtures with epoxy resins exhibit long pot life. The pot life can be defined as the time taken from the initial mixing of the resin and curing agent to the point when the viscosity of the mixture has become so high as to render the mix unusable.3

The cured products with NMA can be designed to have high heat distortion temperatures together with light colour and excellent electrical properties, which need to be maintained at high temperatures; castings can be made with minimal shrinkage, because no by-product is produced during the curing process, and excellent high temperature ageing.4

One limitation of using anhydrides as curing agents is the long and high temperature cure cycles needed to obtain the desired properties of the system. The use of catalysts (a substituted imidazole was used during the work carried out), however, can help to overcome this problem.2
3.1.3.2 Mechanism of epoxy resin cure with anhydrides.

The reaction of an epoxy resin with an anhydride without using a catalyst proceeds slowly even at 200°C. Fisch and Hofmann proposed that a ‘half ester’ is formed when the anhydride ring is opened by secondary alcohols from the epoxy backbone (Figure 3.10, scheme 1). The ‘half ester’ then reacts with an epoxy group to yield the diester (Figure 3.10, scheme 2). However, apart from esterification, etherification occurs as a competitive reaction when using the system phthalic anhydride/epoxy resin. This happens when a secondary alcohol from the backbone of the resin opens an epoxy ring, leading to the formation of β-hydroxy ether (Figure 3.10, scheme 3). This reaction was confirmed by increased epoxy group consumption as compared to diester group formation.

![Scheme 1](image)

![Scheme 2](image)

![Scheme 3](image)

**Figure 3.10.** Mechanism of epoxy resin/anhydride hardener system without using catalyst.

An IR absorption spectroscopy study of these systems by Stevens, concluded that the epoxy resin-anhydride system chemically reacts by consecutive-step addition esterification involving carboxylic acid group intermediates and simultaneous addition etherification in agreement with the mechanism proposed by Fisch and Hofmann.

Tertiary amines are catalysts which affect the course of the anhydride-epoxide reaction. Fischer proposed a mechanism which starts with the activation of anhydride by the amine (Figure 3.11, scheme 1). The formed carboxylate ion reacts with an alkoxide group leading to the formation of the alkoxide ester (Figure 3.11, scheme 2). This alkoxide anion reacts with a new molecule of anhydride, resulting in the formation of the ester.
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(Figure 3.11, scheme 3). Continuation of these alternating sequences produces polyester groups.

![Scheme 1](image1.png)

![Scheme 2](image2.png)

![Scheme 3](image3.png)

**Figure 3.11.** Proposed mechanism by Fischer for the reaction system epoxide/anhydride catalysed with a tertiary amine.9

Tanaka and Kakiuchi10,11 studied the kinetics of the curing reaction of epoxy resin and acid anhydride, and concluded that the reaction between the carboxylate anion and the epoxy resin (Figure 3.11, scheme 2) was the rate-determining step in the curing reaction.11

Lustoň and Maňásek12,13 proposed the formation of allyl alcohol derivates by isomerisation of epoxide (Figure 3.12) and then reaction with the anhydride. Based on conductivity measurements, they found that the active site for the polymerisation is a three-component complex that contains amine, epoxide and anhydride.

\[ NR_3 + R\overset{\text{CH}_2\overset{\text{CH}}{\text{CH}}\text{CH}_2 \rightarrow R\overset{\text{CH=CH-CH}_2\text{-OH}}{\text{CH}_2\overset{\text{CH}}{\text{CH}}\text{CH}_2} \rightarrow NR_3 \]

**Figure 3.12.** Scheme of formation of allyl alcohol from epoxide group.13

Matejka et al.14 studied the mechanism of a model reaction between phenylglycidyl ether (PGE) and benzoic acid anhydride (BAN) catalysed with benzylidimethylamine (BDMA). Different techniques were used to follow the mechanism such as liquid chromatography or NMR spectroscopy. They proposed a different mechanism where initiation consists of
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the reaction of the tertiary amine with the epoxy group, giving rise to a zwitterion that contains a quaternary nitrogen atom and an alkoxide anion (Figure 3.13).

![Figure 3.13. Reaction of epoxide group with a tertiary amine to form a zwitterion](image)

The zwitterion reacts immediately with the anhydride present and forms a salt (Figure 3.14).

![Figure 3.14. Reaction of the zwitterion with the anhydride](image)

In the later stages of the reaction the carboxy anion of the quaternary salt opens the epoxy ring of the next epoxy molecule (Figure 3.15).

![Figure 3.15. Reaction between the carboxy anion and an epoxide group](image)

The alkoxide anion formed in figure 3.15 reacts with a new molecule of anhydride leading to the formation of the diester with simultaneous generation of the carboxy anion (Figure 3.16).

![Figure 3.16. Reaction of alkoxide anion with an anhydride](image)

The overall reaction proceeds with alternative steps: secondary alkoxide anions with anhydrides (Figures 3.14 and 3.16) and the carboxy anion formed from these reactions...
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subsequently opens the epoxide rings (Figure 3.15). A competitive reaction to the co-polymerisation process is when the alkoxide anion reacts with an oxirane group from an epoxy resin molecule (homopolymerisation) leading to an etherification process. The catalyst has a strong influence at this stage, because it can change the balance between esterification and etherification. Bases favour esterification and acids promote etherification$^2$.

3.1.4 Additives to epoxy resins.

A common practice in epoxy resin technology is the use of some particular additives in the reaction system. Sometimes these materials have to be added to the resin-hardener system to modify the properties, e.g., toughness improvement of the cured resin for use in a particular application. The different types of materials that can be added to the system are: diluents, plasticisers, fire retardants, cure accelerators, reinforcements and fillers$^3$.

3.1.4.1 Diluents.

In some systems the viscosity is so high that some liquids need to be used to reduce the viscosity and improve the handling characteristics. There are two types of diluents: reactive (they react chemically with the curing agent and the resin) and non-reactive. They are used in small concentrations, normally between 5-10 phr$^3$.

3.1.4.2 Plasticisers.

In general, cured epoxy resins are quite brittle, and if a more flexible material is needed to resist mechanical stresses, two different modifications can be performed:

- Reactive modification: during the curing process, a long, flexible epoxy resin, hardener or reactive additive may be incorporated into the network system.
- Non-reactive modification: non-reactive long chain molecules may be incorporated into the network remaining unreacted. This type of modification is often referred as plasticisation instead of flexibilisation$^3$. 

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3.1.4.3 Fire retardants.
Traditionally, the incorporation of bromine or chlorine atoms into the system was a technique to improve the fire retardant properties of the epoxy resins. It was often achieved using halogenated epoxy resins or chlorinated curing agents such as blends of chlorendic anhydride/NMA (Figure 3.9).

Brominated epoxy resins and phosphorus containing epoxides\(^{15}\) are currently being used as flame retardants but, due to environmental requirements, the use of non-halogenated flame retardants is an important challenge for the future. Some silicon\(^{16}\) and phosphorus\(^{17}\) containing epoxy resins have been developed with the advantage of the absence of toxic decomposition products when burnt. When heating the system, the silicon component migrates to the surface of the epoxy resin and forms a protective layer with high heat resistance thus avoiding thermal degradation\(^{16}\).

3.1.4.4 Cure accelerators.
These substances can increase the rate of reaction between the epoxy resin and the hardener. In this group of additives, catalysts and co-solvents are included\(^{3}\).

3.1.4.5 Reinforcements.
These additives are inert and fibrous materials, and they are used to increase the strength and stiffness of the epoxy resin system. Glass and carbon are widely used for this purpose\(^{3}\).

3.1.4.6 Fillers.
Fillers are added to the epoxy systems with many different purposes in mind, such as to make the system cheaper or modify some physical and mechanical properties of the system (such as thermal conductivity or hardness)\(^{3}\). The amount of filler that can be added to the resin depends on the viscosity of the resin at the processing temperature.
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Different metal oxides have been found to depress the tensile and compressive strengths, but have little effect on impact stress\(^1\). Silicone-containing additives give the system thermal resistance, dimensional stability and physical strength. More flexible, low thermal expansion, flame resistant, and thermally stable epoxy resin systems have been found using polysiloxanes as additives\(^{16}\). During the experimental work (section 3.2) different ormosils (2\(^{nd}\) chapter) have been added and some mechanical and thermal properties have been investigated.

3.1.5 Properties of epoxy resins.

The large number of different combinations of resins, curing agents and modifiers available makes possible the preparation of cured epoxy systems with a large range of properties.

The main characteristics of an epoxy resin system depend on the molecular structure, dictated by the backbone structures of epoxy resin and curing agent. Also important in the final properties of the system are the extent of crosslinking (it is a measure of the degree of cure), the crosslink density (an increase in the crosslink density would lead to an increase in chemical resistance properties) and the nature of the covalent bond between the epoxy and the hardener (e.g., crosslinking with dicarboxylic anhydrides leads to the formation of polyesters that are resistant to oxidation, but less so to moisture, especially in the presence of basic components)\(^1\).

During the curing process of a given system, it is important to achieve the maximum crosslinking to obtain the most favourable properties. Sometimes, when trapping additives during the curing process, some of this crosslinking can be decreased. To counteract this, a post-cure schedule at higher temperature than the cure temperature is often carried out. By increasing the temperature, the mobility of the molecules in the system will increase, giving immobilised molecules a further opportunity to undergo collision and bond formation\(^2\). Therefore, crosslink density is strongly influenced by the curing temperature (heating increases molecular mobility resulting in higher crosslink
density). As a consequence, after thermal post-curing of the resin, an increase in the chemical resistance properties is often achieved (e.g. anticorrosive coating applications).

Some advantages of using an anhydride as curing agent are: good mechanical and electrical properties, low shrinkage and viscosity, long pot life and little colour. On the other hand, using anhydrides, long cure cycles are needed, in the case of the resin studied in this work 24 hours at 60°C is required.

3.1.5.1 Epoxy resins as thermosetting polymers.

Once the resin has been cured it cannot be converted again into its original form because curing is an irreversible process. This is why epoxy resins are considered as thermosetting polymers (they cannot be re-used by melting and reprocessing). They become permanently hard when heated above a critical temperature and will not soften again on reheating. Further heating will lead to degradation of the material.

From a technological point of view, synthetic polymers can be divided into three main groups according to their stress-strain characteristics: plastics, fibres and elastomers. High modulus and low percentage elongations are the main characteristics of fibres and rigid plastics. They are quite resistant to deformation. On the other hand, elastomers exhibit large reversible elongations under small applied stresses; they have great elasticity. The other group, flexible plastics, presents an intermediate behaviour between these.

Epoxy resin systems can be located in the category of plastics. These are defined as high polymers capable of changing their shape on the application of a force, and retaining these shapes when the force is removed. In other words, the stress has produced a non-reversible strain. These materials can be subdivided into two categories: thermosetting and thermoplastic polymers.

When heated above glass transition temperature \( T_g \), thermoplastic polymers will soften, and they can then be easily moulded. Upon subsequent cooling, they will retain this form.
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The important factor is that when they are heated again, they can be reshaped (if required) before hardening, again upon curing. Therefore it is a cycle that can be carried out several times.

On the other hand, thermosetting polymers become permanently hard when they are heated above a certain temperature, and will not become appreciably softer when reheated. Thermosetting polymers are changed irreversibly from fusible precursors into highly intractable crosslinked resins. Their shaping must be done during the crosslinking process because afterwards it is impossible. They have superior abrasion and dimensional stability characteristics than thermoplastic polymers, which have better flexural and impact properties. Epoxy resin polymers can be located in the thermosetting group\(^{18}\). The high crosslink density which epoxy resins develop during the curing process makes them of a brittle nature. Thermosetting resins have a number of advantages over thermoplastics such as elevated heat distortion temperatures, good solvent resistance and high modulus.

### 3.1.6 Applications of epoxy resins.

The main applications of epoxy resins are in coatings and structural applications, but, in general, the possible uses of these resins result from the variety of properties found. They show excellent adhesion to a variety of substrates; outstanding chemical and corrosion resistance; excellent electrical insulation; high tensile, flexural, and compressive strengths; good thermal stability; a wide range of curing temperatures; and low shrinkage upon cure\(^1\). Because of this wide range of different characteristics, epoxy resins have been employed in very different industries. A brief review of the applications is presented below. For further information an excellent review is presented elsewhere\(^3\).

#### 3.1.6.1 Coatings.

The high mechanical strength and good adhesion of the epoxy resins to many substrates make them ideal for use as durable coatings. Different resin systems with solvent and chemical resistance are obtained by curing at a wide range of temperatures. The higher the temperature, the better the resistance was found to solvents and corrosives\(^1\).
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The 'ideal' epoxy resin system to use it as a coating paint is one which:
- can be applied over the surface as quickly as possible at minimum cost
- has a cheap starting material
- has a long usable life under working conditions
- has the required protection characteristics over the substrate
- is environmentally friendly without containing toxic substances

One of the main uses of epoxy resins as coatings is as anti-corrosive paints, in marine coatings, as coatings for steel pipes for transporting natural gas and as powder coatings in the paint industry to avoid atmospheric pollution due to the solvents used in conventional paints.

3.1.6.2 Laminates and composites.

Laminates and composites can be defined as fibre-reinforced polymers, and many epoxy resins can be used as fibre-reinforced materials (e.g. for printed wiring boards) because of their excellent adhesion to reinforcements and low shrinkage during curing. They provide the final system with good mechanical and electrical properties, and good thermal, chemical, fatigue and moisture resistance.

The aerospace industry is using graphite fibre reinforced multifunctional epoxy resin composites because of their excellent strength to weight ratios. The use of these composites reduces the final cost because of fuel savings.

3.1.6.3 Castings.

One of the main uses of epoxy resins in the past has been in the electrical industry. The versatile epoxy resin casting techniques make these systems ideal for the production of transformers, insulators, high voltage cable accessories, and similar devices.

During casting, the epoxy resin-hardener system is introduced into a mould containing the electrical component to be insulated. Once the curing process has finished, the insulated component has the shape of the specially designed mould.
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In electronics, encapsulation consists in encasing an electronic component in an epoxy resin-based system. One of the drawbacks of this method is that the heat generated when the resin is cured must be controlled; otherwise damage can be produced to the electrical equipment. One of the advantages of using anhydrides as hardeners is that the exotherm is not very high (and therefore the equipment is going to survive the process), and, in addition, the viscosity and shrinkage are low and pot life long. As a consequence of their properties resins cured with anhydrides are used in castings, potting and encapsulation.

3.1.6.4 Construction.
In the construction industry, epoxy systems have been used to improve the performance of traditional materials. They are used in flooring (as the covering material that is frequently placed on top of a sub-floor) and also in roads and bridges to protect from moisture, chemicals and oils. Epoxy resin systems are also used as binders for patios, swimming-pool decks and walks.

3.1.6.5 Adhesives.
Epoxy resin adhesives are used to bond similar and different materials such as metals, glass, ceramics, wood, cloth, and many types of plastics. They can also retain these adhesive properties in a range of temperatures up to 300°C. They have been widely used in the aircraft industry because they can survive at high temperatures and have improved chemical performance compared to conventional materials.

In high molecular weight systems, the large number of hydroxyl groups in the resin backbone improves the adhesive features of the resin.

3.1.7 XLVR16-2 epoxy resin system.
The epoxy resin that has been used during this research work, triglycidyl-\(p\)-aminophenol, was first developed by Union Carbide (previous name Bakelite). It is one of a relatively few epoxy resins containing an aromatic amine with any commercial significance. It is currently marketed by CIBA-GEIGY, and produced by reaction of \(p\)-aminophenol in excess of epichlorohydrin under carefully controlled conditions (Figure 3.17), because it
has a limited thermal stability and polymerises quickly in the presence of a tertiary amine.

A dicarboxylic anhydride (Figure 3.18) was used as a hardener (also called crosslinking agent or curing agent) of the resin. These kinds of hardeners first found use in Europe, but in 1956, a cross-licensing arrangement between most of the basic suppliers opened the anhydride curing agents to widespread application in the electrical industry in the USA.

The anhydride used (nadic methyl anhydride, NMA) offers great versatility, because by altering the resin-curing agent ratio and modifying the cure cycle, several properties of the final system can be altered. When using stoichiometric amounts of NMA and long cure cycles at high temperature, the highest heat resistance and hardness are achieved. On the other hand, an improvement in toughness and crack resistance is obtained by decreasing the amount of anhydride and the cure temperature.

The epoxy resin used during the experimental work is a trifunctional system (three oxirane rings, Figure 3.17), so when cured, it will produce a higher crosslink density and higher glass transition temperature ($T_g$) than difunctional epoxy resins.
3.2 Experimental.

3.2.1 Materials.
XLVR16-2R (trade name of triglycidyl-p-aminophenol) epoxy resin was used as received (Advanced Composite Materials); the epoxy resin was cured using XLVR16-2H (Nadic Methyl Anhydride, NMA, Advanced Composite Materials) as hardener system which contained a substituted imidazole. XLVR16-2 is a low viscosity system (250 mPa·s at 30°C) that allows the resin to be used for RTM (Resin Transfer Moulding) and VARTM (Vacuum Assisted Resin Transfer Moulding). Silicon dioxide (Nyacol Nyasil®20, mean particle diameter: 1.4 μm, from Nyacol Nano Technologies) was used as received.

3.2.2 Instrumentation.
The resin system requires a thermocuring process, so a thermocuring oven (supplied by Pyrotherm Furnaces) was used (2000 W, 400°C maximum).

Glass transition temperature ($T_g$) is characterised by a sudden transition from a hard, glassy or brittle condition to a flexible or elastomeric condition. The glass transition occurs when the polymer molecule chains, normally motionless at temperatures below the glass transition temperature, become free to rotate. Measurements of the $T_g$ of the system were carried out in a Polymer Laboratories dynamic mechanical thermal analyser (Mk II). DMTA technique is based on the application of a small sinusoidal stress to the sample in the form of a torque, push-pull, or a flexing mode, of angular frequency $\omega$. The elastic modulus and the damping characteristics of the polymer can be obtained if it is treated as a classical damped harmonic oscillator.

The strain produced with the application of a sinusoidal stress is the same frequency as, but out of phase with, the stress. It is described by Equation 3.1,

$$\varepsilon^* = \varepsilon_0 \exp(i\omega t)$$  \hspace{1cm} (3.1)

where $\varepsilon^*$ is the strain produced, $\varepsilon_0$ is the maximum amplitude, $\omega$ is the angular frequency ($\omega = 2\pi v$, the frequency is $v$). Equation 3.2 refers to the relationship between the alternating stress and strain,
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\[ \sigma^* = \epsilon^* E^*(\omega) \]  
(3.2)

where \( E^*(\omega) \) is the frequency dependent complex dynamic modulus described by Equation 3.3\(^*\),

\[ E^*(\omega) = E'(\omega) + iE''(\omega) \]  
(3.3)

where \( E'(\omega) \) is the real part of the frequency in phase with the strain called the storage modulus, and \( E''(\omega) \) is the loss modulus, which is defined as the ratio of the component 90° out of phase with the stress. \( E'(\omega) \) represents the amount of stored energy and \( E''(\omega) \) measures the amount of energy dissipated by the material\(^*\).

The phase angle can be calculated from equation 3.4\(^*\). The lost tangent (tan \( \delta \)) represents the damping in the system (the energy loss per cycle).

\[ \tan \delta = \frac{E''}{E'} \]  
(3.4)

At the glass transition temperature (\( T_g \)), \( E'' \) is at a maximum and a decrease of \( E' \) is simultaneously observed. DMTA is a sensitive method to measure \( T_g \) of polymers, and during the present work it was determined from the maximum in the DMTA-plot of tan \( \delta \). Alternatively, the \( T_g \) can also be measured based on the inflection in \( E' \).

The test parameters were standardised during all the testing: combined head, heating rate: 10 K/min, frequency: 10 Hz, strain: 4 %, and temperature range: 30-300°C. The size of the samples was 30x10x1.7 mm.

Differential scanning calorimetry (DSC) (TA Instruments DSC Q100) was also used for determination of glass transition temperature (\( T_g \)). A heating rate of 10 K/min, sample weight of ca. 5 mg and a nitrogen flow of 30 ml/min were maintained for all the experiments. Runs were performed in a temperature range 35-250°C. The \( T_g \) value was calculated using the interactive DSC program (TA Instruments Universal Analysis 2000), picking the inflection point of the break in the heat flow curve. The DSC technique measures the difference in heat flow between the sample pan and an empty reference pan as they are subjected to the same heating rate\(^*\).
Fracture surface morphology was evaluated using a Hitachi S-3200 variable pressure scanning electron microscope. The samples were gold coated using an Edwards Gold Sputter Coating unit to improve conductivity and prevent charging.

Fracture toughness testing was carried out following the standard test method for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials (ASTM D 5045-99)\textsuperscript{21} using compact tension specimens. Samples were prepared by casting the epoxy resin system in silicon rubber moulds with the dimensions 50 mm long by 48 mm high by 6 mm thick (Figure 3.19)\textsuperscript{21}, cured for 24 hours at 60°C and post-cured by ramped heating at 20 K per hour to 175°C and allowing to dwell at this temperature for 2 hours. Holes were mechanically drilled and specimens were pre-cracked using a razor blade. Specimens were tested at QinetiQ using an Instron 5500R tensometer with a 10 kN load cell and a crosshead displacement rate of 2 mm.min\textsuperscript{-1} at room temperature. Three specimens were tested for each sample.

![Figure 3.19. Approximate configuration of fracture toughness test specimen based on ASTM specifications\textsuperscript{21}](image)

3.2.3 Procedure.

In a typical experiment, epoxy resin (XLVR16-2R, 2.5 g, 0.009 moles) and hardener (XLVR16-2H, 3.13 g, 0.018 moles) were mixed at room temperature with the appropriate concentration of ormosil (0, 5, 10 or 20 phr) using a mechanical stirrer for ca. 30 minutes. When mixed, the mixture was cast in aluminium moulds of 30x10x1.7 mm. The system was cured for 24 hours at 60°C, then ramped at 20 K per hour to 175°C and allowed to
dwell at this temperature for 2 hours (post-curing). Finally the films were cooled to room temperature.

3.3 Results and discussion.

Cured epoxy resin systems have one main drawback: they have a considerable brittleness leading to poor fracture toughness, poor resistance to crack propagation, and low impact strength. For some applications which require high strength, such as reinforced plastics, matrix resins for composites and coatings, the inherent brittleness has limited their usage. Therefore, much effort has been made in the last few decades to improve the mechanical properties of epoxy resins, especially their toughness.

In the past, inorganic fillers (silica particles) have been used for the reinforcement of epoxy resins, improving their mechanical properties. Another way of reinforcing the epoxy resin is producing organic-inorganic hybrids by in situ reaction of TEOS (inorganic source of the hybrid) with epoxy resins (organic source). A different way of modifying the properties of the resin could be the use of organic-inorganic hybrids as non-reactive fillers.

During this work, the addition of previously synthesised organic-inorganic hybrids (2nd chapter) to a particular epoxy resin system, and the change in some of the resin properties due to this, have been explored. Resins with high glass transition temperature tend to be very brittle (due to their high level of crosslinking). It was thought that addition of a material with both organic and inorganic nature would improve the toughness of the resin whilst maintaining its excellent thermal and mechanical properties.

3.3.1 Use of ormosils as additives to XLVR16-2 epoxy resin system.

Some of the ormosils produced during previous work (see 2nd chapter) were added to the epoxy resin system. The cure and post-cure cycles were the same as explained in section 3.2.3 and the \( T_g \) of the resulting product was measured using DMTA and DSC techniques. The results obtained are summarised in Table 3.1.
## Chapter 3: Use of ormosils as additives to epoxy resins

Table 3.1. Results of using ormosils as additives to XLVR16-2 epoxy resin system.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Epoxy resin (XLVR16-2R)</th>
<th>Hardener (XLVR16-2H)</th>
<th>Ormosil (from 2nd chapter) as filler (phr)</th>
<th>$T_g$ (°C) using DMTA</th>
<th>$T_g$ (°C) using DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>-</td>
<td>222</td>
<td>190</td>
</tr>
<tr>
<td>48</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr of MeSi$_{1.7}$O$_3$ (Brij® 98, exp. no. 20)</td>
<td>217</td>
<td>174</td>
</tr>
<tr>
<td>49</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr of MeSi$_{1.7}$O$_3$ (Brij® 98, exp. no. 20)</td>
<td>206</td>
<td>172</td>
</tr>
<tr>
<td>50</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.50 g, 20 phr of MeSi$_{1.7}$O$_3$ (Brij® 98, exp. no. 20)</td>
<td>200</td>
<td>165</td>
</tr>
<tr>
<td>51</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr of MeSi$_{1.7}$O$_3$ (Brij® 98, exp. no. 20)</td>
<td>232</td>
<td>204</td>
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<tr>
<td>52</td>
<td>2.5 g</td>
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<td>197</td>
</tr>
<tr>
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<td>2.5 g</td>
<td>3.13 g</td>
<td>0.50 g, 20 phr of MeSi$_{1.7}$O$_3$ (Brij® 98, exp. no. 23)</td>
<td>223</td>
<td>190</td>
</tr>
<tr>
<td>54</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr of MeSi$_{1.7}$O$_3$ (20 % polystyrene, exp. no. 41)</td>
<td>217</td>
<td>184</td>
</tr>
<tr>
<td>55</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr of MeSi$_{1.7}$O$_3$ (20 % polystyrene, exp. no. 41)</td>
<td>214</td>
<td>186</td>
</tr>
<tr>
<td>56</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.50 g, 20 phr of MeSi$_{1.7}$O$_3$ (20 % polystyrene, exp. no. 41)</td>
<td>212</td>
<td>186</td>
</tr>
<tr>
<td>57</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr of MeSi$_{1.7}$O$_3$ (Ultra Turrax®, exp. no. 11)</td>
<td>220</td>
<td>181</td>
</tr>
<tr>
<td>58</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr of MeSi$_{1.7}$O$_3$ (Ultra Turrax®, exp. no. 11)</td>
<td>212</td>
<td>176</td>
</tr>
<tr>
<td>59</td>
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<td>0.50 g, 20 phr of MeSi$_{1.7}$O$_3$ (Ultra Turrax®, exp. no. 11)</td>
<td>209</td>
<td>157</td>
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<tr>
<td>60</td>
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<td>3.13 g</td>
<td>0.125 g, 5 phr of EtSi$_{1.7}$O$_3$ (Ultra Turrax®, exp. no. 12)</td>
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<td>182</td>
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<tr>
<td>61</td>
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<td>0.25 g, 10 phr of EtSi$_{1.7}$O$_3$ (Ultra Turrax®, exp. no. 12)</td>
<td>214</td>
<td>184</td>
</tr>
<tr>
<td>62</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.50 g, 20 phr of EtSi$_{1.7}$O$_3$ (Ultra Turrax®, exp. no. 12)</td>
<td>203</td>
<td>145</td>
</tr>
<tr>
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<td>3.13 g</td>
<td>0.125 g, 5 phr of MeSi$_{1.7}$O$_3$ (Brij® 52, exp. no. 31)</td>
<td>211</td>
<td>194</td>
</tr>
<tr>
<td>64</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr of MeSi$_{1.7}$O$_3$ (Brij® 52, exp. no. 31)</td>
<td>206</td>
<td>161</td>
</tr>
<tr>
<td>65</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr of EtSi$_{1.7}$O$_3$ (Brij® 52, exp. no. 32)</td>
<td>201</td>
<td>184</td>
</tr>
<tr>
<td>66</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr of EtSi$_{1.7}$O$_3$ (Brij® 52, exp. no. 32)</td>
<td>200</td>
<td>180</td>
</tr>
<tr>
<td>67</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr of PhSi$_{1.7}$O$_3$ (Brij® 52, exp. no. 33)</td>
<td>204</td>
<td>183</td>
</tr>
<tr>
<td>68</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr of PhSi$_{1.7}$O$_3$ (Brij® 52, exp. no. 33)</td>
<td>202</td>
<td>182</td>
</tr>
</tbody>
</table>

a. parts per hundred of the resin.
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After the curing and post-curing, amber coloured films were obtained (the larger the amount of ormosil, the darker the colour of the film). Good results in the dispersion of the ormosil within the resin were found, as will be shown in fracture surface experiments (section 3.3.5). When using a non-polar solvent (such as one with long alkyl chains) for the synthesis of ormosils (2nd chapter), the organic content was oriented towards the solvent, and the inorganic material would form the nucleus of the hybrid particles. As a result of this distribution, good compatibility between both components (ormosil and epoxy resin) was found. Hence, ormosil particles were well dispersed within the epoxy resin matrix.

The values obtained using DSC were about 30-35°C lower than those from DMTA measurement (Table 3.1). The DSC $T_g$ value is normally lower than the DMTA value determined by $\tan \delta_{\text{max}}$ because for the latter analysis a larger amount of product is necessary than for the former, so more heat is needed to reach the transition temperature, thus shifting the $T_g$ to higher apparent temperatures. Also in DMTA analyses there is frequency dependence because the stress applied to the sample is with a frequency $\omega$. The transition temperatures are found to shift to increased temperatures with increased frequencies (during the experiments carried out, the frequency used was 10 Hz, and normally this value is in the range of 0.1-1 Hz). DMTA is approximately 1000 times more sensitive than DSC, in terms of baseline deflection, for detecting $T_g$ and produces more useful mechanical property data, though larger product size is required for carrying out the measurement.

The unmodified resin specimen (exp. no. 47) was repeated several times and the $T_g$ was measured in each case in an attempt of studying the reproducibility of the DMTA technique. All glass transition temperatures were obtained in a range of 2°C, and similar dynamic modulus and internal friction plots were obtained (Figures 3.20 and 3.21). Therefore, DMTA was confirmed as a good technique for the collection of thermal and mechanical data from the experiments.
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Figure 3.20. Dynamic modulus of three samples of XLVR16-2 epoxy resin system with no filler.

Figure 3.21. Internal friction (tan δ) of three samples of XLVR16-2 epoxy resin system with no filler.

In the majority of the experiments a reduction of the $T_g$ was observed when the filler was added to the epoxy resin (Table 3.1). The larger the amount of ormosil added, the lower the $T_g$ observed. It was thought that the filler caused impediment to network formation, producing a decrease in the crosslink density of the system (plasticising effect). Therefore, because the degree of crosslinking is lower, the ‘rubber state’ of the resin is reached at lower temperatures, leading to lower $T_g$ for the material.

The case of using methyl-modified silica (produced with Brij® 98, see 2nd chapter) as additive to the epoxy resin system is going to be discussed as a model of general behaviour for ormosils as additives to epoxy resins. Figures 3.22 and 3.23 represent the dynamic modulus and internal friction respectively.
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Figure 3.22. Dynamic modulus of XLVR16-2 epoxy resin system using different amounts of MeSi_{1.75}O_{3} (Brij® 98) as additive.

The curves of the dynamic modulus (Figure 3.22) have the shape characteristic of crosslinked amorphous polymers in the transition region\(^25\). When increasing the amount of filler within the resin, a decrease of the dynamic modulus in the transition and rubbery regions is observed (Figure 3.22). The dynamic modulus (E') is related to the epoxy network density\(^26\), so the degree of crosslinking of the epoxy resin system is deduced to be lower when the amount of filler (ormosil) is increased because of the lower values obtained for the dynamic modulus.

Figure 3.23 Internal friction (tan \(\delta\)) of XLVR16-2 epoxy resin system using different amounts of MeSi_{1.75}O_{3} (Brij® 98) as additive.

The internal friction reflects the amount of energy dissipated as heat during the deformation of the material. An increase of tan \(\delta\) was observed when the amount of ormosil filler was increased (Figure 3.23). The increase in tan \(\delta\) reflects the increasing ability of the polymer to absorb energy as the molecular constraints are reduced. The
lower degree of crosslinking when the system is richer in additive (plasticising effect) leads to a greater mobility of chain segments in the polymer.

DSC curves of the products of the experiments discussed above (experiments 47-50), showed the characteristic drop in heat flow caused by the change from a glassy to a rubbery state (Figure 3.24). The $T_g$ was measured from the inflection point of the heat flow curve.

![DSC measurements of XLVR16-2 epoxy resin system using different amounts of MeSi$_{1.75}$O$_3$ (Brij® 98) as additive.]

The behaviour of the $T_g$ was observed to be the same during DSC experiments as in DMTA analyses (Figure 3.24). When the concentration of the ormosil (filler) increases, the glass transition temperature shifts to lower temperatures. This decrease in $T_g$ values can be attributed to an increase in the mobility of chain segments of epoxy resin because of the lower degree of crosslink density when fillers are added.

The ormosil particles (filler) are thought to impede the crosslinking reactions between epoxy resin and hardener proceeding to completion. As a consequence of this, lower crosslink density in the cured epoxy resin was expected. In a typical DSC experiment, during the first scan the sample 53 (Table 3.1) (from 35 to 250°C at 10 K/min), showed an exothermic transition (Figure 3.25). This transition could be due to some uncured
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material that is reacting due to heating during the DSC experiment. When a re-scan is
carried out, this exothermic transition disappears (Figure 3.25) because the material is
already fully cured with the heat applied during the first scan. The T_g is expecting to
increase from first to second scan because further curing of the resin takes place during
the first scan leading to a higher crosslink density. Thus, it was demonstrated that there
was some uncured material still present in the sample, which means that the crosslink
density was lower than when using the resin with no filler. The resin starts to degrade at
ca. 270°C, so this is why all the DSC analyses were performed in the range of 35 to
250°C (so thermal decomposition was avoided).

Figure 3.25. DSC measurements of XLVR16-2 epoxy resin system using 20 phi of MeSi_{1.75}O_3
(Brij® 92) as additive (exp. no. 53).

3.3.2 Use of silicon dioxide as additive to XLVR16-2 epoxy resin system.

It was thought that the different organic content of the hybrids used as fillers was going to
play an important role in the final properties of the particulate-filled resin. With this goal
in mind, a series of ‘baseline’ experiments were carried out using silicon dioxide (Nyacol
Nyasil®20) as filler in different concentrations in the epoxy resin (Table 3.2). Therefore, a
comparison of the effect of using different organic content (methyl-, ethyl-, phenyl- and
no organic group) in the silica particles could be achieved.
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The reference composite XLVR16-2R/XLVR16-2H/silicon dioxide was prepared by mechanical blending of the silica Nyasil®20 with the reaction mixture in different concentrations (Table 3.2). Curing and post-curing processes were carried out as explained in section 3.2.3.

Table 3.2. Results of using silicon dioxide as additive to XLVR16-2 epoxy resin system.

<table>
<thead>
<tr>
<th>Exp. no</th>
<th>Epoxy resin (XLVR16-2R)</th>
<th>Hardener (XLVR16-2H)</th>
<th>Filler (phr*)</th>
<th>$T_g$ (°C) using DMTA</th>
<th>$T_g$ (°C) using DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>-</td>
<td>222</td>
<td>190</td>
</tr>
<tr>
<td>69</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr of SiO₂ (Nyasil®20)</td>
<td>204</td>
<td>180</td>
</tr>
<tr>
<td>70</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr of SiO₂ (Nyasil®20)</td>
<td>203</td>
<td>176</td>
</tr>
<tr>
<td>71</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.50 g, 20 phr of SiO₂ (Nyasil®20)</td>
<td>192</td>
<td>169</td>
</tr>
</tbody>
</table>

*parts per hundred of the resin.

Very good dispersion of the filler particles in the resin matrix was obtained in these experiments (69-71) as would be shown in fracture surface analyses (section 3.3.5). When the concentration of the filler was increased, a drop in the glass transition temperature was observed. It was thought that the predominant effect could be the interference of the particles in the hardener-resin reaction proceeding to completion, leading to a lower degree of crosslinking and a shift of the $T_g$ to lower temperatures (Table 3.2).

Internal friction of XLVR16-2 resin system with 5 phr of different alkyl-modified silicas is shown in Figure 3.26, so the effect of different organic substituents in the filler could be compared.
During the synthesis of ormosils (2\textsuperscript{nd} chapter), the most successful method was using Brij\textsuperscript{®} 52 as surfactant. The particles obtained (section 2.3.4.4) were spherical in the case of the methyl-modified silica. When dispersing these particles within the epoxy resin matrix, a good dispersion was obtained as observed by the reduction of the area of tan $\delta$ in the glass transition region (Figure 3.26). The good dispersion of the filler hinders the movement of the polymer chains leading a decrease in the area of the tan $\delta$. On the other hand, the particles of other ormosils (ethyl- and phenyl-modified silicas) were not spherical, and not such a good dispersion was achieved, noting the tan $\delta$ in the transition area. Tan $\delta$ becomes larger showing an increase in the mobility of the polymer chain segments from lowering of the degree of crosslinking of the resin system.

In the case of silicon dioxide, because there is no organic moiety in the filler, the compatibility with the epoxy material is lower than in the case of methyl-modified silica, even though the SiO$_2$ particles are small in diameter (1.4 $\mu$m) and it could be some compatibility through Si-OH groups. Thus, the tan $\delta$ is bigger and appears at lower temperatures than in the case of the methyl-ormosil. Figure 3.27 shows a chart with the different glass transition temperatures obtained for the products of these experiments (47, 63, 65, 67 and 69).
In figure 3.27, a decrease in the $T_g$ is observed for the resin system when 5 phr of filler has been added. The smaller decrease was produced using methyl-modified silica (exp. no. 63) because of the good distribution of spherical particles within the matrix as has been explained before. In the rest of the cases, the compatibility between filler and resin was not as good, either because of the size and aggregation of the particulate-filler (ethyl- and phenyl-modified silica, experiments 65 and 67), or because of the absence of organic material bridging the epoxy resin with the inorganic material (silicon dioxide, exp. no. 69).

### 3.3.3 Use of surfactants as additives to XLVR16-2 epoxy resin system.

During the synthesis of ormosils in the previous work (2nd chapter), different surfactants were used in an attempt to stabilise the ‘pseudo-dispersion’ when hybrid particles were being formed. The effect of these surfactants on the epoxy resin properties was studied by blending different amounts of surfactant with the epoxy resin system (Table 3.3). Curing and post-curing processes were carried out as explained in section 3.2.3.
Table 3.3. Results of using surfactants as additives to XLVR16-2 epoxy resin system.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Epoxy resin (XLVR16-2R)</th>
<th>Hardener (XLVR16-2H)</th>
<th>Filler (phr(^a))</th>
<th>(T_g) (°C) using DMTA</th>
<th>(T_g) (°C) using DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr Brij(^a) 92</td>
<td>209</td>
<td>165</td>
</tr>
<tr>
<td>73</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr Brij(^a) 92</td>
<td>191</td>
<td>142</td>
</tr>
<tr>
<td>74</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.50 g, 20 phr Brij(^a) 92</td>
<td>169</td>
<td>126</td>
</tr>
<tr>
<td>75</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr Brij(^a) 98</td>
<td>199</td>
<td>165</td>
</tr>
<tr>
<td>76</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr Brij(^a) 98</td>
<td>198</td>
<td>161</td>
</tr>
<tr>
<td>77</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.50 g, 20 phr Brij(^a) 98</td>
<td>186</td>
<td>141</td>
</tr>
</tbody>
</table>

\(a.\) parts per hundred of the resin

As expected, a large decrease in the \(T_g\) was observed when the amount of ‘filler’ was increased (Table 3.3). The surfactant molecules are long alkyl chains (Figure 3.28), so they interfere with the crosslinking reactions between resin and hardener, lowering the degree of crosslinking and, therefore, shifting the \(T_g\) to lower temperatures. The surfactants act as plasticisers to the hardener-resin network.

![Figure 3.28. Structures of surfactants Brij\(^a\) 92 and Brij\(^a\) 98.](image)

However, during the synthesis of ormosils, the usual amount of surfactant used was 5% based on the total weight of reactants (see 2\(^{nd}\) chapter). Therefore, when using 5, 10 or even 20 phr of filler, the maximum amount of surfactant present in the filler was 0.006, 0.012 and 0.024 g respectively. The largest value represents less than 1 phr when blending the filler with the resin, so small amounts of surfactants are not expected to affect the properties of the final system significantly.

3.3.4 Use of silsesquioxanes as additives to XLVR16-2 epoxy resin system.

The silsesquioxanes made in DMSO obtained in previous work (2\(^{nd}\) chapter) were investigated as fillers to the XLVR16-2 epoxy resin system. Resin, hardener and filler
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were mechanically blended in different concentrations (Table 3.4); cure and post-cure cycles were carried out as explained in section 3.2.3.

Table 3.4. Results of using silsesquioxanes as additives to XLVR16-2 epoxy resin system.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Epoxy resin (XLVR16-2R)</th>
<th>Hardener (XLVR16-2H)</th>
<th>Ormosil (from 2nd chapter) as filler (phr)</th>
<th>( T_g (^\circ C) ) using DMTA</th>
<th>( T_g (^\circ C) ) using DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr of Me(_2)Si(_3)O(_3) (exp. no. 42)</td>
<td>223</td>
<td>191</td>
</tr>
<tr>
<td>79</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr of Me(_2)Si(_3)O(_3) (exp. no. 42)</td>
<td>221</td>
<td>185</td>
</tr>
<tr>
<td>80</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.50 g, 20 phr of Me(_2)Si(_3)O(_3) (exp. no. 42)</td>
<td>223</td>
<td>191</td>
</tr>
<tr>
<td>81</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr of Et(_2)Si(_3)O(_3) (exp. no. 42)</td>
<td>219</td>
<td>187</td>
</tr>
<tr>
<td>82</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr of Et(_2)Si(_3)O(_3) (exp. no. 43)</td>
<td>216</td>
<td>185</td>
</tr>
<tr>
<td>83</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.50 g, 20 phr of Et(_2)Si(_3)O(_3) (exp. no. 43)</td>
<td>224</td>
<td>190</td>
</tr>
<tr>
<td>84</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr of Hex(_2)Si(_3)O(_3) (exp. no. 44)</td>
<td>219</td>
<td>188</td>
</tr>
<tr>
<td>85</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr of Hex(_2)Si(_3)O(_3) (exp. no. 44)</td>
<td>219</td>
<td>190</td>
</tr>
<tr>
<td>86</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.50 g, 20 phr of Hex(_2)Si(_3)O(_3) (exp. no. 44)</td>
<td>222</td>
<td>187</td>
</tr>
<tr>
<td>87</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr of Ph(_2)Si(_3)O(_3) (exp. no. 45)</td>
<td>216</td>
<td>187</td>
</tr>
<tr>
<td>88</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr of Ph(_2)Si(_3)O(_3) (exp. no. 45)</td>
<td>220</td>
<td>188</td>
</tr>
<tr>
<td>89</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.50 g, 20 phr of Ph(_2)Si(_3)O(_3) (exp. no. 45)</td>
<td>219</td>
<td>186</td>
</tr>
<tr>
<td>90</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.125 g, 5 phr of SiO(_2) from DMSO (exp. no. 46)</td>
<td>213</td>
<td>175</td>
</tr>
<tr>
<td>91</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.25 g, 10 phr of SiO(_2) from DMSO (exp. no. 46)</td>
<td>225</td>
<td>186</td>
</tr>
<tr>
<td>92</td>
<td>2.5 g</td>
<td>3.13 g</td>
<td>0.50 g, 20 phr of SiO(_2) from DMSO (exp. no. 46)</td>
<td>212</td>
<td>176</td>
</tr>
</tbody>
</table>

a. parts per hundred of the resin.

The dispersion of the silsesquioxanes within the resin matrix was not uniform, and phase separation occurred between resin and filler. Two different layers could be observed in the 1.7 mm thick films obtained, probably because of a problem of compatibility. The synthesis of silsesquioxanes was undertaken using DMSO as the oxygen donor (2nd chapter), which is a much more polar solvent than the one used for the synthesis of the ormosils previously used (a mixture of toluene and petroleum-ether). As a consequence
of this, when silsesquioxane particles were being formed, the inorganic material was oriented towards the polar solvent, while the non polar content of the hybrid (organic content of the silsesquioxanes) was orientated towards the core of the particles. Thus, the surface polarity of the silsesquioxane particles is governed by the inorganic network of the hybrid, which is not entirely compatible with the epoxy resin system. This incompatibility was thought to be the reason why two different layers were obtained.

Therefore, glass transition temperature analyses (Table 3.4) were not thought to be reliable since the filler material was not well distributed through the epoxy resin network.

### 3.3.5 Fracture Surfaces.

The fracture surfaces of particulate-filled epoxy resins were analysed by the SEM method, which provides some information about the dispersion of these particles within the epoxy resin matrix.

![Figure 3.29. SEM pictures of fracture surface of XLVR6-2 epoxy resin system with no filler (left) and with 20 phr of silicon dioxide (right).](image)

The fracture surface of the resin samples shows how the additive affects the dispersion in the epoxy matrix. In figure 3.29, on the left hand side, the epoxy resin matrix without any filler is shown. The lines observed are called crack propagation lines. On the right hand side (Figure 3.29), the epoxy resin network is modified by Nyasil®20, but no evidence of SiO₂ aggregates is observed (the silica particles did not aggregate together to form silica domains). During the blending process, the silicon materials were uniformly dispersed
through the resin network. Good miscibility was also observed when studying the fracture surface of the XLVR16-2 epoxy resin system filled with 5 phr of methyl-modified silica (Brij\textsuperscript{®} 98, exp. no. 48, figure 3.30).

Figure 3.30. SEM picture of fracture surface of XLVR6-2 epoxy resin system with 5 phr of methyl-modified silica produced with Brij\textsuperscript{®} 98 as additive (exp. no. 48).

3.3.6 Fracture toughness.

Fracture toughness is an important parameter for moulding resins because it measures the resistance of a material to failure from fracture starting from a pre-existing crack. Epoxy resins are inherently brittle because of their highly crosslinked structure, and they are often filled to improve their mechanical performance, and, in particular, to improve their fracture toughness. A traditional way of toughening epoxies is the addition of elastomers (carboxyl-terminated co-polymer of butadiene and acrylonitrile liquid rubber) into the polymeric matrix\textsuperscript{27}; the rubber acts as centres of dissipation of mechanical energy leading to an improvement in the fracture resistance of the system. Silicone rubber has been used as toughening agent with no damage to the good thermal properties of the system\textsuperscript{28}. However, phase separation was found between silicone and epoxy resin because of incompatibility problems\textsuperscript{28}. These problems were expected to be overcome with the use of organic-inorganic hybrids as fillers, where the organic content helps to increase the filler-resin compatibility, and the inorganic part acts as the real toughening agent. Some of the ormosils produced in previous work (2\textsuperscript{nd} chapter, experiments 31-33) were
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investigated as toughening agents to the XLVR16-2 epoxy resin system in different concentrations (5 and 10 phr).

The fracture toughness of the epoxy resin systems was investigated and for the calculation of the critical stress intensity factor, $K_{ic}$, compact tension analyses were carried out. The $K_{ic}$ property characterises the resistance of a material to fracture in a neutral environment in the presence of a sharp crack under severe tensile constraint\(^{21}\). For calculation of $K_{ic}$, three fundamental measurements of the specimen were necessary: the thickness ($B$), the crack length ($a$) and the width ($W$). $K_{ic}$ was calculated in MPa.m\(^{1/2}\) units from the following expression (Equation 3.5)\(^{21}\):

$$K_{ic} = \left( \frac{P_0}{BW^{1/2}} \right) f(x)$$

(3.5)

where $f(x)$ is:

$$f(x) = \frac{(2 + x)(0.886 + 4.64x - 13.32x^2 + 14.72x^3 - 5.6x^4)}{(1 - x)^{3/2}}$$

(3.6)

where:

- $P_0$ = load at crack initiation in kN,
- $B$ = specimen thickness in cm,
- $W$ = specimen width in cm,
- $a$ = crack length in cm and
- $x = a/W$

The resin was modified using silicon dioxide (Nyasil\(^{20}\)) as additive in different concentrations (0, 5 and 10 phr) and fracture toughness analysis results are shown in Figure 3.31. A typical value of $K_{ic}$ for an epoxy polymer (ca. 0.6 MPa.m\(^{1/2}\))\(^{29}\) was obtained by measuring the unmodified specimen.
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Figure 3.31. Compact tension results of XLVR16-2 epoxy resin system using different concentrations of SiO$_2$ (Nyasil®20) as additive.

The fracture toughness of the resin system increased (within the boundaries of the errors) when adding silicon dioxide as toughening agent (Figure 3.31). During previous work, it was found that the fracture toughness of silicone-modified systems increased with a decrease in the diameter of the silicone phase$^{28,30}$. Even though silicones and silica behave different, the increase in the fracture toughness of the resin system could be due to the uniform dispersion of the filler within the matrix because of the small size of the silica particles (1.4 μm in diameter). These products showed that the commercial silica Nyasil®20 can be directly used as inorganic fillers in the preparation of epoxy-silica hybrid materials improving the fracture toughness of the system.

Figure 3.32. Fracture toughness of the XLVR16-2 resin system versus SiO$_2$ content.

The major improvement in the fracture toughness of the system (50 % greater than that of the unmodified resin) was produced when 5 phr of silicon dioxide were used as filler.
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When this concentration was increased above 5 phr, the fracture toughness dropped, but considering the error bars, this decrease is not very big (Figure 3.32 shows a different way of representing the variation of $K_\text{ic}$). Therefore, the toughening efficiency is most effective for the blends with approx. 5 phr of silicon dioxide (Nyasil®20) as filler.

The particle size of the silicon phase of the filler was found to be an important factor in the fracture toughness of epoxy resins. Therefore, a selection of the smallest-particulate ormosils obtained during past work (2nd chapter) was investigated as toughening agents for epoxy resins. The results obtained for the specimens containing different concentrations (0, 5 and 10 phr) of methyl-modified silica (from exp. no. 31, 2nd chapter) are shown in Figure 3.33:

![Figure 3.33](image)

**Figure 3.33.** Compact tension results of XLVR16-2 epoxy resin system using different concentrations of MeSi$_{1.75}$O$_3$ (Exp. no. 31 from 2nd chapter) as additive.

The variation of the critical stress intensity factor ($K_\text{ic}$) as a function of the concentration of the filler (MeSi$_{1.75}$O$_3$) in phr shown in Figure 3.33 indicates that $K_\text{ic}$ does not change considerably.

When 5 phr of EtSi$_{1.75}$O$_3$ (from exp. no. 32, 2nd chapter) were added, the fracture toughness of the system was about 50 % greater than that of the unmodified resin (Figure 3.34). However, the addition of 10 phr of the same filler led to a slight decrease of the fracture toughness (within the boundaries of the errors) in comparison with the 5 phr specimen, but still higher than that of the unmodified resin (ca. 40 % greater).
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Figure 3.34. Compact tension results of XLVR16-2 epoxy resin system using different concentrations of EtSi_{1.75}O_{3} (from exp. no. 32, 2nd chapter) as additive.

In the case of using phenyl-modified silica (from exp. no. 33, 2nd chapter) as an additive to the XLVR16-2 epoxy resin, a slight decrease of the fracture toughness was found when 5 phr of filler (Figure 3.35) were used. On the other hand, when 10 phr of PhSi_{1.75}O_{3} was added, the fracture toughness was about 40 % greater than that of the unmodified resin (note the large error band).

Figure 3.35. Compact tension results of XLVR16-2 epoxy resin system using different concentrations of PhSi_{1.75}O_{3} (from exp. no. 33, 2nd chapter) as additive.

3.4 Conclusions.

This study describes an attempt to modify a selected epoxy resin system (XLVR16-2 epoxy resin) using organically modified silicates (ormosils) as additives. The resin investigated is a trifunctional system (triglycidyl-\(\)-aminophenol), thus, when cured, a three-dimensional network with high crosslink density is formed. Highly crosslinked
Chapter 3: Use of ormosils as additives to epoxy resins

epoxy resins are known as brittle thermosetting polymers which need to be toughened for various applications. Some of the ormosils produced in previous work (2nd chapter) have been investigated as toughening agents.

The viscosity of the epoxy resin when it was blended with these ormosils did not appear to increase drastically, maintaining the excellent handing conditions of the resin. This is an important factor to take into account since the systems developed here are for use in resin injection technologies (XLVR16-2 epoxy resin is a VARTM system).

Fracture surface studies of the cured systems showed that the ormosil particles did not aggregate together during the blending process. The ormosil additives were uniformly dispersed throughout the resin matrix.

Using ormosils as additives, some mechanical properties of the epoxy resin have been improved (fracture toughness), but some thermal properties have been lowered (decrease in T_g). Therefore, to enhance the mechanical properties without sacrificing the thermal ones, the filler size and concentration have to be carefully chosen. The biggest improvement in the fracture toughness (about 50 % greater than that of the unmodified resin) was produced using 5 phr of ethyl-modified silicate (exp. no. 65) as additive. However, this improvement was approx. the same as when 5 phr of pure silica was used as toughening agent (Figure 3.31).

DMTA analyses revealed a decrease in the glass transition temperatures of the resin with ormosils as additives, which might be due to the plasticising effect of the ormosil particles in the epoxy network, resulting in a lowering of the crosslink density.

Ormosils with different organic content were tested as additives. Methyl-modified silicates were found to be the fillers that showed the lowest decrease in the T_g of the system. When ormosils with larger organic groups were investigated, a bigger decrease in the T_g was found. This could be due to a greater plasticising effect when the size of the
organic moiety is increased. Thus, the crosslink density of the resin was lowered with the increase in the size of the organic group of the ormosil.

The amount of filler added was also found to be an important factor in the $T_g$ of the resin. The higher the concentration of ormosil, the larger the plasticising effect observed.
3.5 References.

Chapter 3: \textit{Use of ormosils as additives to epoxy resins}

Chapter 4

Emulsion Polymerisation of Polyhedral Oligomeric Silsesquioxanes
Chapter 4: Emulsion Polymerisation of Polyhedral Oligomeric Silsesquioxanes

4.1 Introduction.

4.1.1 Silsesquioxanes.
Silsesquioxanes are defined as silica or silicate networks that are modified by the covalent attachment of organic groups, with each silicon atom covalently bonded to one organic group\(^1\). The different structures of silsesquioxanes have been reported as random structure, ladder structure, cage structure, and partial cage structure\(^2\) (Figure 4.1).

![Figure 4.1. Structures of silsesquioxanes\(^2\).](image)

4.1.2 Polyhedral oligomeric silsesquioxanes (POSS).
Polyhedral oligomeric silsesquioxanes (POSS) are a unique class of compounds because of their chemical composition and physical nature. POSS reagents consist of an inorganic silica-like core cage that is surrounded by organic substituents (Figure 4.2) where \(R\) can be a number of organic groups (functional or inert). POSS reagents have the empirical formula \((RSiO_{1.5})_n\), \(n=6\) (I), \(n=8\) (II), \(n=10\) (III), \(n=12\) (IV) (Figure 4.2), and they were first reported in 1946\(^3\).

![Figure 4.2. Structural representation of POSS reagents\(^4\).](image)

POSS cages are formed by a rigid, thermally stable silicon-oxygen framework that contains an oxygen to silicon ratio of 1.5 (their name is derived from the non-integer, one and one-half or *sesqui*, ratio between oxygen and silicon atoms, \(SiO_{1.5}\))^5. The prefix
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'oligo' (Greek oligos, "few") is often used to indicate a small number of silsesquioxane links. The inorganic core is surrounded by a hydrocarbon layer enabling solubilisation in organic solvents and/or polymerisation of these systems. The variety of substituents that can be incorporated on the silicon atom has attracted the interest of many researchers, focusing on the incorporation of a polymerisable group on one of the silicon atoms. This is combined with aliphatic hydrocarbon functionality on the remaining silicon atoms to achieve desirable solubility properties.

The synthesis of oligosilsesquioxanes is based on the hydrolytic polycondensation of \( RSiX_3 \), where \( R \) is a chemically stable organic substituent and \( X \) is a highly reactive substituent, such as a chlorine or alkoxy group (Equation 4.1)\(^4,6\).

\[
\begin{align*}
nRSiX_3 & + 1.5nH_2O \rightarrow (RSiO_{1.5})_n + 3nHX \\
\end{align*}
\] (4.1)

The polycondensation process of \( RSiX_3 \) is a multistep process which is strongly dependent on several factors such as the concentration of initial monomer in the solution; nature of the solvent; character of substituent \( R \) in the initial monomer; nature of functional group \( X \) in the initial monomer; type of catalyst employed; temperature; rate of addition of water and quantity of water added; and solubility of the polyhedral oligomers formed\(^4\).

4.1.2.1 Synthesis of functionalised POSS monomers.

The synthesis of functionalised POSS monomers is based on the corner capping of incompletely condensed POSS-trisilanols \( (R_7Si_7O_9(OH)_3) \) with a variety of silane coupling agents\(^7\). The process leads to the formation of fully condensed POSS monomers \( (R_7Si_8O_{12}Y) \) containing seven non-reactive \( R \) substituents and with only one corner functionalised for further polymerisation reactions (Figure 4.3).
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Figure 4.3. Scheme of corner capping of an incompletely condensed POSS-trisilanol with a silane coupling agent.

Using this method, different families of functionalised POSS reagents have been produced, such as \( R_7\text{Si}_8\text{O}_{12}\)-acrylcs, \( R_7\text{Si}_8\text{O}_{12}\)-olefins\(^8\), \( R_7\text{Si}_8\text{O}_{12}\)-silanes, \( R_7\text{Si}_8\text{O}_{12}\)-styrenes, or \( R_7\text{Si}_8\text{O}_{12}\)-epoxides\(^7,9\) (Figure 4.4).

Figure 4.4. POSS monomers produced from POSS trisilanol precursors.

The corner capping of incompletely condensed POSS trisilanol{s is the most general synthesis process for POSS silicon-oxygen frameworks. The synthesis of incompletely condensed POSS-trisilanol{s \( (R_7\text{Si}_7\text{O}_9\cdot\text{OH})_3 \) is based on the hydrolytic condensation reaction of alkyltrichlorosilane by refluxing in aqueous acetone (Figure 4.5)\(^10,11,12\). A variety of substituents can be incorporated in the corners of the cage, upon selection of different alkyl groups attached to the silicon chloride (there are many commercial alkyltrichlorosilanes available).

Figure 4.5. Scheme of synthesis of incompletely condensed POSS-trisilanol{s.\(^10,12\)
Incompletely condensed POSS-trisilanols have also been investigated as ligands to prepare heterogeneous metallasilsesquioxanes\(^{13,14}\). The chemistry of metallasilsesquioxanes could be used as a model for the silica-supported metal catalysts\(^{14}\). They exhibit a strong tendency to undergo reactions to fill the vacant corner with a large number of metals such as Ge, Sn or Zr\(^{12}\).

Functionalised POSS reagents can also be produced on a truly large scale and a large variety of functionalisation is accessible through the controlled cleavage of Si-O-Si linkages from \(\text{(C}_6\text{H}_{11})_8\text{Si}_8\text{O}_{12}\) with stoichiometric amounts of triflic acid (trifluoromethanesulfonic acid, TfOH)\(^{15,16}\). The ditriflates produced during the first step can be subsequently hydrolysed to incompletely condensed silsesquioxanes (Figure 4.6), which can be the starting point to a large variety of different functionalised POSS reagents.

A similar pathway (cleavage of a single Si-O-Si linkage in \(\text{R}_8\text{Si}_8\text{O}_{12}\)) has been developed involving the base catalysed hydrolysis, under stoichiometric control, of fully condensed POSS (Figure 4.7)\(^{17,18}\).

POSS macromers can participate in a variety of common transformations, such as polymerisation or grafting reactions\(^{19}\). For example, POSS-olefins can be transformed
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into POSS-epoxides using standard organic techniques (epoxidation of vinyl-substituted POSS with meta-chloroperoxybenzoic acid [m-CPBA]\(^{20}\), Figure 4.8).

Another example is the use of R\(_7\)Si\(_8\)O\(_{12}\)H macromers in hydrosilylation reactions to afford a graftable source of POSS during the modification reactions of various vinyl-containing reagents and polymers\(^8\).

4.1.2.2 POSS-methacrylate monomers.

POSS-methacrylates possess a hybrid organic-inorganic three-dimensional structure which contains from one to eight methacrylate groups. The most common POSS-methacrylates have seven non-reactive organic groups and one methacrylate group, and they can be incorporated into thermoplastics by co-polymerisation processes. Multifunctional methacrylates of this type can be used as effective crosslinking agents.

In the present work, the POSS molecules used [(RSi\(_{1.5}\)O\(_5\))\(_n\)] have \(n=8\) (cage-like), with seven ethyl substituents and one methacrylate group (methacryl ethyl-POSS). Eight methacrylate groups are the substituents in the other sample (methacryl-POSS cage mixture).

Monofunctionalised POSS-methacrylate monomers are typically prepared via the corner capping reaction of incompletely condensed POSS trisilanols (R\(_7\)Si\(_7\)O\(_9\)(OH)\(_3\)) with appropriately functionalised silane coupling reagents (Figure 4.9)\(^{21}\).
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Figure 4.9. Synthesis of POSS-methacrylate monomers via corner capping reactions\textsuperscript{21}.

An alternative method to prepare POSS-methacrylate monomers is shown in figure 4.10. It is based in the nucleophilic substitution of a POSS-chloride derivate with methacrylic acid.

![Figure 4.10. Synthesis of POSS-methacrylate monomers from R(\text{SiO}_{1.5})_8\text{Cl} and methacrylic acid\textsuperscript{21}.](image)

POSS-methacrylate monomers have several desirable physical properties such as good solubility in common organic solvents, such as THF, toluene, chloroform and hexane\textsuperscript{9,21}. They can also be easily polymerised using standard free radical or anionic techniques. POSS-reagents improve polymer properties such as thermal stability, glass transition temperature, heat distortion temperature, and oxygen permeability when used as modifiers in several thermoplastics\textsuperscript{7}.

### 4.1.2.3 Polymerisation of POSS monomers.

Polymers containing POSS reagents are a novel class of hybrids that are thought to impart greater thermal and mechanical stability to a material\textsuperscript{22}. The inclusion of bulky inorganic groups such as POSS macromers gives the resultant polymers their unusual structure and properties.
POSS-based hybrid polymers can be divided into three main groups: ‘star-type’ architecture, ‘bead-type’ architecture and ‘pendant-type’ architecture\(^{23}\). The first category (‘star-type’) involves POSS cages that contain multifunctional (i.e. more than two) polymerisable groups. These functional groups can form three-dimensional network materials, with the drawback of insolubility in common organic solvents. In the second category (‘bead-type’), the POSS cage is incorporated into the backbone of the polymer by two functional groups. The third category (‘pendant-type’, figure 4.11) is based on a single functional POSS reagent that can be used as monomer or co-monomer in standard methods of polymerisation.

![Figure 4.11. Representation of POSS-polymer with ‘pendant-type’ architecture\(^{24}\).](image)

The synthesis of polymers containing POSS reagents has been reported using conventional free-radical polymerisation techniques\(^{7,9,24,25}\), condensation polymerisation\(^{5}\), ring-opening metathesis polymerisation (ROMP)\(^{26,27,28,29}\), and atom transfer radical polymerisation (ATRP)\(^{22,30,31}\).

### 4.1.2.4 Polymerisation of POSS-methacrylate monomers.

The methacrylate group in this type of POSS monomer permits the polymerisation under standard free-radical conditions of these monomers. A polymerisation study was done under typical homogeneous polymerisation conditions which includes the use of 2,2’-azobis(isobutyronitrile) (AIBN) as initiator and toluene as solvent (Figure 4.12)\(^{19}\).
Despite the bulkiness of POSS-methacrylate monomers which might hinder or prevent their polymerisation, these systems easily polymerised under the conditions described above^{19}. The differences in the alkyl substituents on the POSS cage affected the solubility of the polymers but did not influence their relative thermal stabilities, which were observed to be very high, with POSS-methacrylate polymers decomposing at 388°C without melting^{19}. Compared to the decomposition temperature of poly(methyl methacrylate) (PMMA) (it begins depolymerisation to methyl methacrylate above 200°C and quantitatively yields monomer at 350-400°C), the POSS-methacrylate decomposition temperature was high^{19}. DSC and TMA studies showed no thermal transitions (from 0 to 400°C) for the POSS-methacrylate polymers, in contrast to the typical thermal transitions of PMMA (105°C for atactic, 160°C for syndiotactic, and 43°C for isotactic). The apparent absence of a glass transition in POSS-methacrylate polymers might reflect the overall rigid nature of the methacrylate polymer backbone resulting from the dominant Si₈O₁₂-cage pendant groups, leading to a reduction of segmental mobility^{19}.

Methacrylate-containing POSS polymers have been also produced by ATRP, yielding homopolymers, ABA triblock and AB star diblock co-polymers (Figure 4.13)^{22,30}. 

**Figure 4.12.** Free-radical polymerisation scheme of POSS-methacrylate monomer^{19}. 

\[ R = \text{cyclohexyl or cyclopentyl} \]
4.1.2.5 Applications of POSS monomers.

The hybrid organic-inorganic nature together with nanosized cage structures make POSS reagents interesting additives to thermoplastics, modifying the composition, local structure and chain mobility of these polymeric systems\(^{32}\).

Generally, the inclusion of POSS macromers during polymerisation changes the thermal properties of the polymers obtained towards more thermally resistant systems. The glass transition temperature of the polymer is also enhanced upon co-polymerisation with the
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associated POSS monomer\textsuperscript{33}. These enhancements have been shown to apply to a variety of thermoplastics systems, such as poly(methyl methacrylate)\textsuperscript{19,22,30}, polystyrene\textsuperscript{24,34}, polyethylene\textsuperscript{27}, polynorbornene\textsuperscript{26,28,29} or polyurethane\textsuperscript{35} and a few thermosetting systems such as epoxy resins\textsuperscript{32}. In this last case, a monofunctional epoxy-substituted POSS monomer (Figure 4.14) was incorporated into a network formed by two epoxy monomers, diglycidyl ether of bisphenol-A (DGEBA) and 1,4-butanediol diglycidyl ether (BDGE) at a DGEBA/BDGE 9:1 molar ratio\textsuperscript{32}. The diamine-terminated poly(propylene oxide) (Jeffamine D230) was used as the hardener in an amount which gave a 1:1 equivalent of epoxy to amine functions\textsuperscript{32}. Upon increase of the amount of the monofunctional POSS epoxy into the network, the glass transition temperature was observed to increase without an increase in the degree of crosslinking within the network. This was thought to be due to the nanoscopic size of these POSS cages and their ability to hinder the motion of the molecular chains and network junctions\textsuperscript{32}.

![Figure 4.14. Structure of monofunctional epoxy-substituted POSS monomer.](image)

Another example of enhancement of the thermosetting properties, such as thermal dimensional stability, with the use of POSS monomers was upon incorporation of the multifunctional POSS monomer (C\textsubscript{6}H\textsubscript{5}CHCHO\textsubscript{4}-(Si\textsubscript{8}O\textsubscript{12})-(CH=CHC\textsubscript{6}H\textsubscript{5})\textsubscript{4}) (Figure 4.15) into an aliphatic, low viscosity epoxy network\textsuperscript{36}.

![Figure 4.15. Structure of multifunctional POSS monomer.](image)
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The same POSS monomer with four β-substituted styrenes and four epoxidised styrenes (Figure 4.15) was co-polymerised with styrene and blended with vinyl ester resin\textsuperscript{37}. The $T_g$ of 5 and 10 wt. % incorporated POSS monomer-styrene co-polymers blended with the resin were higher than that of the pure polystyrene blended with the resin\textsuperscript{37}. This was due to the crosslinking induced by the POSS monomer (Figure 4.15) and to the restriction of segmental motion by the bulky POSS moieties\textsuperscript{37}.

Blending studies of POSS-methacrylate homopolymers and co-polymers (POSS-methacrylate + methyl methacrylate) with PMMA have been carried out to determine the effects of blending on the properties of thermoplastic PMMA\textsuperscript{7}. POSS-methacrylate was homopolymerised and co-polymerised with methyl methacrylate using free-radical conditions. Co-polymerisation of POSS-methacrylate with MMA resulted in a resin that showed a greatly enhanced miscibility with PMMA in comparison to that of POSS-methacrylate homopolymer with PMMA. Blends of PMMA with the POSS-methacrylate/MMA co-polymer showed the glass transition temperature 100°C higher than that for PMMA and their decomposition temperatures were also higher\textsuperscript{7}.

It has been reported that blending POSS into polymers such as PMMA increases the mechanical strength of the system, thereby improving the overall properties of the materials\textsuperscript{38}. POSS co-polymers show promise for applications such as windshields or flame retardant polymer composites\textsuperscript{38}.

Liquid-crystalline (LC) monomers have also been co-polymerised with POSS macromers under typical free-radical conditions\textsuperscript{39}. The thermal stability of the hybrid polymers was increased upon an increase of the POSS content. The $T_g$ of the co-polymer was higher in comparison with that of the (LC) homopolymer because of the reduction of segmental mobility in the hybrid polymer, which was caused by the incorporation of hard, compact POSS moieties\textsuperscript{39}.
4.1.3 Free-radical polymerisation of methacrylate monomers.

Methacrylate monomers (Figure 4.16) are versatile building blocks for polymers because they are readily polymerised or co-polymerised with a variety of other monomers. The nature of the R groups together with the molecular weight of the polymer determines the properties and behaviour of the polymer.

The free-radical polymerisation of methacrylate monomers follows the typical chain mechanism that proceeds in three different stages: (i) Initiation, which involves the generation of the active centre that acts as a chain carrier; (ii) Propagation, which involves the growth of the macromolecular chain by repeated addition of the monomer to the chain and is controlled by a kinetic chain mechanism; (iii) Termination, which is when the growth of the chain is brought to a halt by neutralisation or transfer of the active centre.

4.1.3.1 Initiation.

An initiator undergoes homolytic fission into radials that must be stable enough to react with a monomer and start the polymerisation process. There are several reactions to produce radicals such as thermal decomposition, photolysis, redox reactions and ionizing radiation.

4.1.3.2 Propagation.

In this stage, the monomer reacts with the free radical and a chain carrier is formed. A macromolecular structure is then formed by a chain propagation process (Figure 4.17).
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\[ \text{CH}_3 + \text{H}_2\text{C}==\text{C}==\text{C}==\text{O} \text{CH}_3 \rightarrow \text{CH}_2\text{C}==\text{C}==\text{C}==\text{O} \text{CH}_3 \]

Figure 4.17. Scheme of chain propagation of free-radical polymerisation of MMA.

4.1.3.3 Termination.

Termination of chain propagation can happen in different ways such as interaction of two active chain ends, reaction of an active chain end with an initiator radical, transference of the active centre to another molecule in the system, or interaction with impurities (e.g. oxygen) or inhibitors. The most important process of all of them is the interaction between two chain ends. There are two possible routes: combination, where two chain ends couple together, and disproportionation, which leads to an unsaturated group and two dead polymer chains (Figure 4.18).

Figure 4.18. Scheme of the most important termination reactions.
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4.2 Experimental.

4.2.1 Materials.
Methyl methacrylate monomer (MMA) (Aldrich) 99 % came with some inhibitors (such as hydroquinones). To purify the monomer, it was passed through a short column of Al₂O₃ (basic alumina) (Fischer-Scientific). Inhibitors and acidic impurities were thus eliminated⁴². The obtained MMA was then degassed by bubbling with dry nitrogen gas for 30 minutes and subsequently stored at 0°C before use. The purity of the monomer was confirmed by ¹H NMR spectroscopy.

Methacryl ethyl-POSS (MA 0717, Hybrid Plastics) and methacryl-POSS cage mixture (MA 0735, Hybrid Plastics) monomers were used as received.

Tween® 20 (Acros Organics), sodium n-dodecyl sulphate (SDS) (Lancaster), Brij® 30 (Aldrich) and DB-110A (antifoam emulsion based on PDMS) (Dow Corning) were used as received.

The redox system for the initiation of the polymerisation process was formed by potassium persulfate (K₂S₂O₈) (99 %) (Aldrich) as the water soluble initiator, and sodium hydrosulfite (Na₂S₂O₄) (99 %) (Aldrich) as the accelerator of the redox process. Both reagents were used as received.

4.2.2 Instrumentation.
Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer interfaced with a Perkin-Elmer computer (PE-Spectrum v2.00 software was used). Samples were prepared as explained in section 2.2.2 (2nd chapter). Abbreviations used to describe absorptions are as follows: vs= very strong; s= strong; m= medium; w= weak; vw= very weak; b= broad; sp= sharp and sh= shoulder.

Surface morphology was evaluated using a Hitachi S-3200 variable pressure scanning electron microscope. Prior to mounting, samples were gold coated using an Edwards Gold Sputter Coating unit to prevent charging under the electron beam. The morphology
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of the products was also investigated using a Philips 400T transmission electron microscope. Samples were cast from aqueous medium and mounted on carbon mesh Cu TEM grids (Agar Scientific).

Thermal properties were characterised on a differential scanning calorimeter from TA Instruments (DSC Q100). A heating rate of 10 K/min, sample weight of ca. 5 mg and a nitrogen flow of 30 ml/min were maintained for all the experiments.

$^1$H NMR spectra were obtained on Bruker AM-300 MHz and Bruker DRX-500 MHz instruments operating at 300.13 MHz and 500.15 MHz respectively. Samples were dissolved in CDCl$_3$ and TMS was used as reference.

Elemental analyses were kindly carried out by Ms Nicola Walker at the University of Surrey on a Leeman Laboratories Inc. CE 440 Elemental Analyser.

Freeze-drying was employed to separate the polymer particles from the emulsions. Samples were freeze-dried overnight in a Heto FD 3 freeze-drier.

4.2.3 Procedure.

4.2.3.1 Emulsion polymerisation of MMA using Tween® 20 as surfactant.

In a typical experiment, poly(methyl methacrylate) (PMMA, exp. no. 94) was formed by polymerising previously purified MMA (see section 4.2.1). In a flask containing 20 ml of water, MMA (0.5 g, 5 mmol), Tween® 20 (0.05 g, 10 % of monomer weight) and DB-110A (0.05 g, 10 % m. w.) were dispersed using a magnetic stirrer at room temperature. After 15 minutes, potassium persulfate (0.01 g, 2 % m. w.) and sodium hydrosulfite (0.002 g, 20 % initiator weight) were added to the flask. The emulsion was then stirred with a magnetic stirrer under a dry nitrogen atmosphere for 4 hours at 85°C. The latex obtained was freeze-dried overnight leading to a white powder that was washed with water and filtered to remove the surfactant and the inorganic salts. The product was then dried in a vacuum oven at 60°C for 8 hours yielding 0.72 g of PMMA as product. $^1$H NMR spectroscopy (in CDCl$_3$) (ppm): 3.60 (s, 3 H), 1.82 (m, 2 H) and 0.95 (m, 3H). FT-
4.2.3.2 Emulsion polymerisation of MMA using SDS as surfactant.

Polymerisation of MMA (Exp. no. 97) was carried out by dispersing the previously purified monomer (3 g, 30 mmol) in 20 ml of water using sodium dodecyl sulphate (SDS) (0.06 g, 2 % m. w.) as surfactant. The dispersion of the monomer was carried out using an ultrasonic bath during 1 hour at room temperature under nitrogen atmosphere. Then, the initiator, potassium persulfate (0.03 g, 1 % m. w.), was added to the system; the resulting oil-in-water emulsion was heated at 85°C for 6 hours under steady stirring (mechanical stirrer) under a slow stream of nitrogen. After cooling the latex, PMMA was precipitated by dropping the latex in 100 ml of methanol and stirred for 30 minutes. The mixture was then centrifuged for 20 minutes at 2000 rev./min and the white precipitate obtained was washed with water and centrifuged again (20 minutes at 2000 rev./min). The product was then washed twice with methanol (50 ml) centrifuging after every wash (15 minutes at 2000 rev./min) and then dried in a vacuum oven at 60°C for 8 hours yielding 2.76 g (92 %) of PMMA as product. [*H NMR spectroscopy (in CDCl₃) (ppm): 3.59 (s, 3 H), 1.81 (m, 2 H) and 0.85 (m, 3H). FT-IR spectroscopy showed absorptions at: v_max. (cm⁻¹): 2996-2952 (m, b); 1724 (vs, sp); 1435 (m, b) and 1140 (vs, sp)].

4.2.3.3 Emulsion polymerisation of methacryl ethyl-POSS monomer.

In exp. no. 98, methacryl ethyl-POSS monomer (3.74, 5 mmol) and SDS (0.08 g, 2 % m. w.) were dispersed in 20 ml of water using an ultrasonic bath for 1 hour under a nitrogen atmosphere. Potassium persulfate (0.04, 1 % m.w.) was then added and the dispersed system was then mechanically stirred under nitrogen flow at 85°C for 86 hours. Poly(methacryl ethyl-POSS) was precipitated by dropping the latex in 100 ml of methanol and stirred for 30 minutes. The mixture was then centrifuged for 20 minutes at 2000 rev./min and the white precipitate obtained was washed with water and centrifuged again (20 minutes at 2000 rev./min). The product was then washed twice with methanol (50 ml) centrifuging after every wash (15 minutes at 2000 rev./min). The product obtained was dried in a vacuum oven for 8 hours at 60°C and 1.92 g (51 %) of
poly(methacryl ethyl-POSS) was obtained as a white powder. Typical $^1$H NMR spectra (in CDCl$_3$) of monomer (starting material) and polymer (final product) are shown in Figures 4.26 and 4.27 (section 4.3.2.1). FT-IR spectroscopy showed absorptions at: $v_{\text{max.}}$ (cm$^{-1}$): 2960-2890 (m, b); 1722 (m, sp); 1460 (w, sp), 1250 (m, sp); 1070 (vs, sp) and 750 (m, sp).

4.2.3.4 Emulsion co-polymerisation of methacryl ethyl-POSS monomer with MMA.

In exp. no. 100, co-polymerisation of methacryl ethyl-POSS (1.87 g, 2.5 mmol) and MMA (0.25 g, 2.5 mmol) was carried out by dispersing both monomers in 20 ml of water using SDS (0.04 g, 2 % of total weight of co-monomers) as surfactant. The system was dispersed using an ultrasonic bath during 1 hour at room temperature under nitrogen atmosphere. Then, potassium persulfate (0.02 g, 1 % of total weight of co-monomers) was added to the system; the resulting emulsion was heated at 85°C for 86 hours under mechanical stirring and under a slow stream of nitrogen. After cooling the latex, the co-polymer was precipitated by dropping the latex in 100 ml of methanol and stirred for 30 minutes. The mixture was then centrifuged for 20 minutes at 2000 rev./min and the white precipitate obtained was washed with water and centrifuged again (20 minutes at 2000 rev./min). The product was then washed twice with methanol (50 ml) centrifuging after every wash (15 minutes at 2000 rev./min) and then dried in a vacuum oven at 60°C for 8 hours yielding 2.01 g (95 %) of co-polymer methacryl ethyl-POSS + MMA (1:1 molar ratio). Typical $^1$H NMR spectrum (in CDCl$_3$) of the co-polymer obtained is shown in Figure 4.34 (section 4.3.2.2). FT-IR spectroscopy showed absorptions at: $v_{\text{max.}}$ (cm$^{-1}$): 2968-2880 (m, b); 1722 (s, sp); 1461 (m, sp), 1253 (m, sp); 1080 (vs, sp); 758 (m, sp) and 693 (s, sp).

4.3 Results and discussion.

4.3.1. Emulsion polymerisation of MMA.

In the first part of the work, emulsion polymerisation conditions for the formation of PMMA were optimised, before moving on to the polymerisation of methacrylate POSS
reagents. The main components in an emulsion polymerisation system are a water-insoluble monomer, an aqueous phase containing surfactant, and a water-soluble initiator. All the ingredients are mixed at the beginning of the reaction, and an oil-in-water emulsion is formed. The polymerisation process is usually initiated by thermal degradation of the initiator to produce free radicals that will react with the monomer. Chain polymerisation then leads the formation and growth of latex particles. These polymer particles form a colloid stabilised against coalescence by surfactant that is present on the surface of the particles.

The first initiator investigated was a redox system that was used for polymerisation of MMA at low temperature in previous work by the Polymer Group at the University of Surrey\(^4^3\). This system is based on a mixture of oxidising (potassium persulfate, \(\text{K}_2\text{S}_2\text{O}_8\)) and reducing (sodium hydrosulfite, \(\text{Na}_2\text{S}_2\text{O}_4\)) agents, and produces \textit{in situ} free-radical intermediates. By using redox initiator systems, polymerisations are affordable at much lower temperatures (25-60°C) than thermally initiated systems (75-90°C). The reaction mechanism between initiator (persulfate) and accelerator (sulfur salt) is not fully understood, but it leads to the formation of a pair of radicals (Equation 4.2), and one of them, the sulfate radical, will act as the initiator of the polymerisation process\(^4^3\).

\[
\text{S}_2\text{O}_8^{2^-} + \text{S}_2\text{O}_3^{2^-} \rightarrow \text{SO}_4^{-} + \text{SO}_4^{2-} + \text{S}_2\text{O}_3^{-}
\]  

(4.2)

In a typical emulsion polymerisation, a surfactant is used to stabilise the monomer droplets and the particles of polymer when formed. Tween\(^\text{®}20\) was used for this type of polymerisation in previous work\(^4^3\) because it led to stable emulsions. As a consequence of the use of surfactants in stirred emulsions, the production of foam (dispersion of a gas in a liquid or a solid) could be a problem in the final structure of the particles formed. A possible solution for foam production was suggested\(^4^3\): the use of an antifoam agent able to spread at the air-liquid interface. A commercial antifoam agent (DB-110 A) based on polydimethyl siloxane (PDMS) was used for this purpose. The inorganic and organic content gives to PDMS a very low surface energy, so it can penetrate the air-liquid interface, making PDMS-based antifoam agents very powerful as foam breakers.
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In experiment 93, previously purified MMA was added to a flask which contained water, Tween® 20, DB-110 A, potassium persulfate and sodium hydrosulfite. The emulsion was stirred with a magnetic stirrer under dry nitrogen (inert atmosphere) for 20 hours at room temperature.

Polymerisation of MMA was carried out under nitrogen atmosphere because the presence of O₂ in the reaction medium may lead to side reactions (Figure 4.19), which would result in a decrease in the polymerisation rate.

![Figure 4.19](image)

**Figure 4.19.** Scheme of inhibitory effect caused by copolymerisation of oxygen with monomer.⁴⁰

The chain continued to propagate until all the monomer in the system had been consumed leading to a polymeric structure similar to Figure 4.20.

![Figure 4.20](image)

**Figure 4.20.** Structure of a chain of poly(methyl methacrylate).

The length of the chain depends on the concentration of the radical initiator. Because radicals are very reactive, they tend to interact as quickly as possible to form inactive covalent bonds. Thus, when the initiator concentration is high, short chains will be produced; on the other hand, when the concentration is low, long chains will be formed.⁴¹

After 20 hours of polymerisation, the latex formed was freeze-dried overnight. A white powder was obtained, which was washed with water and filtered and then dried in a vacuum oven at 60°C for 8 hours yielding 1.06 g of PMMA as product. [¹H NMR spectroscopy (in CDCl₃) (ppm): 3.66 (s, 3 H), 1.81 (m, 2 H) and 0.90 (m, 3H). FT-IR spectroscopy showed absorptions at: ν<sub>max</sub> (cm⁻¹): 2950 (m, b); 1725 (vs, sp); 1437 (m, b) and 1140 (vs, sp)].
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The yield obtained in the polymerisation at room temperature was very low, thus for the next experiment (Exp. no. 94) the temperature was increased to 85°C. The procedure is described in section 4.2.3.1. The yield obtained at this temperature was over 100 % (section 4.2.3.1), which can be due to the presence of some impurities within the product. Freeze drying (which is a dehydration method where the water in the sample is frozen and then removed by sublimation) was used for the isolation of the product; therefore, impurities from the emulsion (such as salts from initiator and accelerator, surfactant and antifoam) could still be present in the powder obtained. As a consequence of this the yield was over 100 %.

In subsequent experiments, the use of freeze drying for isolating the product from the latex was avoided. In exp. no. 95, MMA, Tween® 20, DB-110 A, K₂S₂O₈ and Na₂S₂O₄ were added to 20 ml of water. The procedure for the formation of the latex was similar to that used before (section 4.2.3.1). Once the latex was formed, PMMA was precipitated by dropping the latex in 100 ml of methanol and stirred the mixture for 30 minutes. The solid product was then filtered using a 1.6 μm pore diameter glass microfibre filter (Whatman) and then dried in a vacuum oven at 60°C for 8 hours. The product obtained was PMMA (0.17 g, 34 %). [¹H NMR spectroscopy (in CDCl₃) (ppm): 3.60 (s, 3 H), 1.81 (m, 2 H) and 0.98 (m, 3H). FT-IR spectroscopy showed absorptions at: vₘₐₓ. (cm⁻¹): 2976-2946 (m, b); 1723 (vs, sp); 1432 (m, b) and 1141 (vs, sp)].

The yield was quite low, and it was thought to be due to incomplete polymerisation. Thus, the reaction time was increased in subsequent experiments, from 4 hours to 6 hours. The production of foam during the emulsion was not a problem for the latex targeted here, and because the use of the antifoam agent (DB-110 A) was adding PDMS impurities to the products obtained, it was not used anymore during the production of subsequent latices. Different surfactants were also investigated (Figure 4.21); Brij® 30, a non-ionic surfactant with different structure to Tween® 20, and sodium n-dodecyl sulphate (SDS), an anionic surfactant which is typically used in emulsion polymerisations⁴⁴. Also the amount of surfactant was reduced from 10 % to 2 % in
monomer weight, as 5-2 % m.w. is the typical amount of stabiliser used in emulsion polymerisations when the particle size of the latex is around 1 \( \mu \text{m} \)\(^{45}\).

Figure 4.21. Structure of Tween\(^{\circledast} 20\), Brij\(^{\circledast} 30\) and SDS.

Once the temperature of the reaction was increased to 85\(^\circ\)C, the presence of a redox system as initiator was no longer necessary; this is because the persulfate undergoes thermal degradation at ca. 50\(^\circ\)C yielding the necessary radicals to initiate the polymerisation (Figure 4.22)\(^{44}\).

Figure 4.22. Scheme of thermal degradation of potassium persulfate.

However, a secondary reaction of these radicals with water may produce hydroxyl radicals (Equation 4.3), which may be the true initiators\(^{45}\).

\[
\text{SO}_4^{-} + \text{H}_2\text{O} \rightarrow \text{HSO}_4^{-} + \text{HO}^{\cdot}
\]

Equation 4.3

In order to achieve a further purification of the product, the isolation system was also modified. The latices obtained in subsequent products were precipitated by dropping them into methanol and stirring for 30 minutes. The systems were then centrifuged for 20 minutes at 2000 rev./min and the precipitates obtained were washed with water and centrifuged again (20 minutes at 2000 rev./min). The products were then washed twice with methanol, centrifuging after every wash (15 minutes at 2000 rev./min). In previous experiments no washing process was carried out, so the chance of having impurities was higher.

A final variation to the process was carried out in the method of mixing the components of the emulsion. Up until this point, the components of the emulsion system were mixed with a magnetic stirrer, and if fine particles are desired, a higher shear stirrer may be
required. In subsequent experiments, monomer and surfactant were added to the aqueous medium and mixed using an ultrasound bath for one hour under nitrogen atmosphere. Thus, the monomer should be very well dispersed in the aqueous medium and stabilised with the surfactant. Once the initiator was added to the system, the emulsified system was stirred vigorously using a mechanical stirrer during the polymerisation process.

In experiments 96 and 97, two different surfactant systems were investigated as mentioned above. The details and results of these experiments are summarised in Table 4.1 and the procedure of both experiments were as described in section 4.2.3.2.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Monomer (MMA)</th>
<th>Surfactant</th>
<th>Initiator (K₂S₂O₈)</th>
<th>React. time</th>
<th>Yield</th>
<th>^1H-NMR (ppm) (CDCl₃)</th>
<th>IR absorptions (cm⁻¹) (approximate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>96</td>
<td>3 g, (30 mmol)</td>
<td>Brij® 30</td>
<td>0.03 g (2 % m. w.)</td>
<td>6 hours</td>
<td>1.61 g (54 %)</td>
<td>3.60 (s, 3 H), 1.61 (m, 2 H) and 0.85 (m, 3H)</td>
<td>2986-2947 (m, b), 1722 (vs, sp), 1432 (m, b) and 1142 (vs, sp)</td>
</tr>
<tr>
<td>97</td>
<td>3 g, (30 mmol)</td>
<td>SDS</td>
<td>0.03 g (2 % m. w.)</td>
<td>6 hours</td>
<td>2.76 g (92 %)</td>
<td>3.59 (s, 3 H), 1.81 (m, 2 H) and 0.85 (m, 3H)</td>
<td>2996-2952 (m, b), 1724 (vs, sp), 1435 (m, b) and 1140 (vs, sp)</td>
</tr>
</tbody>
</table>

The main difference between latices formed with both surfactants (Brij® 30 and SDS) was the stability of the polymer colloid. The dispersion of the SDS-latex was stable, whilst the Brij® 30-latex coagulated leading to a two phase system, solid particles of PMMA and aqueous medium. Therefore, SDS was found to be the better stabiliser for this emulsion system. Also upon using SDS as surfactant, a higher yield was found than using Brij® 30.

Scanning electron microscopy (SEM) was used to analyse the particle morphology of both PMMA products (white powders) using Brij® 30 and SDS (Figure 4.23). Spherical PMMA particles were obtained in both experiments, although the use of SDS as surfactant lead to much smaller particles (ca. 50 nm in diameter) than when using Brij® 30 (ca. 150-200 nm).
However, it was thought that the isolation method of the polymer could have an influence over the morphology of the final particles. Therefore, transmission electron microscopy (TEM) analyses were carried out on the latices formed after the polymerisation took place. Before dropping the latex into methanol to precipitate the polymer, a couple of droplets of each latex sample (experiments 96 and 97) were settled in a copper grid and they were left at room temperature for 2 days, until the water had evaporated and a very fine powder remained on the grid. The results are shown in Figure 4.24.

Figure 4.23. SEM pictures of PMMA formed using Brij® 30 (left) and SDS (right) as surfactants.

Figure 4.24. TEM pictures of PMMA latices formed using Brij® 30 (left) and SDS (right) as surfactants.

TEM analyses showed spherical PMMA particles of ca. 50 nm in diameter when the surfactant used to stabilise the emulsion during the polymerisation process was SDS (Figure 4.24, right). On the other hand, the Brij® 30-latex was not very well stabilised, as mentioned above, leading to phase separation. The majority of the polymer was within...
the solid phase and not much PMMA was present in the aqueous phase, as can be seen in
the TEM picture (Figure 4.24, left), which was taken from the aqueous phase of the latex.
Therefore, SDS was chosen as stabiliser for further emulsion polymerisations of POSS
reagents.

Elemental analysis was done in the most successful of the PMMA experiments (Exp. no.
97) to corroborate the purity of the product. The figures obtained were in close agreement
with the theoretical values (Table 4.2).

<table>
<thead>
<tr>
<th>Elemental analysis</th>
<th>C (%)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st analysis</td>
<td>59.2</td>
<td>8.20</td>
</tr>
<tr>
<td>2nd analysis</td>
<td>59.3</td>
<td>8.23</td>
</tr>
<tr>
<td>Theoretical percentages</td>
<td>60.0</td>
<td>8.05</td>
</tr>
</tbody>
</table>

4.3.2. Emulsion polymerisation of POSS reagents.

4.3.2.1 Homopolymerisation of POSS reagents at 85°C.

Once the conditions of emulsion polymerisation were optimised for MMA, POSS
reagents with methacrylate groups were used as monomers under same conditions as
above. Two main types of reactions were carried out: homopolymerisation of POSS
reagents (Figure 4.25) and co-polymerisation of POSS reagents with MMA (Figure 4.32).

Homopolymerisations of methacryl ethyl-POSS (Exp. no. 98) and methacryl-POSS cage
mixture (Exp. no. 99) were carried out through the methacrylate group present in both
POSS macromers (Figure 4.25). Therefore, the same conditions as applied for emulsion
polymerisation of MMA were investigated here. The procedure carried out was the same
as explained in section 4.2.3.3. Homogeneous free radical polymerisation of methacryl-
POSS reagents has been described previously by Lichtenhan et al.\textsuperscript{19}, where the
polymerisation was carried out over 24 hours. It was thought that an emulsion system
may take longer than a homogeneous system to polymerise, since in the former there are
3 phases (see section 1.2, 1\textsuperscript{st} chapter) and in the latter there is only one phase.
Figure 4.25. Scheme of homopolymerisation of methacryl ethyl-POSS (I) and methacryl-POSS cage mixture (II).

Typical $^1$H NMR spectra (in CDCl$_3$) of methacryl ethyl-POSS monomer (starting material) and poly(methacryl ethyl-POSS) (final product) are shown in Figures 4.26 and 4.27.

Figure 4.26. $^1$H NMR (CDCl$_3$) spectrum of methacryl ethyl-POSS monomer.
Figure 4.27. $^1$H NMR (CDCl$_3$) spectrum of poly(methacryl ethyl-POSS) after 86 hours of polymerisation.

The peaks corresponding to the methacrylate backbone (a and b in Figure 4.27) confirmed the formation of the polymer (the estimated percentage conversion was 97%). However, despite the decrease in the relative intensity of the peaks corresponding to the protons from the double bond and the methyl group attached to a double bond (a and b in Figure 4.26), when polymerisation occurs there is still some unreacted monomer present in the final product which can be seen in Figure 4.27 (3% of the final product). This was confirmed with DSC measurements, where an exotherm was obtained due to further curing of unreacted monomer when heating at ca. 160°C (Figure 4.28).

Figure 4.28. DSC analysis of exp. no. 98 product, poly(methacryl ethyl-POSS).
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The FT-IR spectrum of the polymer obtained (exp. no. 98) showed absorptions at $v_{\text{max.}}$ (cm$^{-1}$): 2960-2890 (m, b) from C-H stretching vibrations; 1722 (m, sp) from C-O vibrations; 1460 (w, sp) from C-H bending vibrations; 1250 (m, sp) from Si-Et symmetric deformations; 1070 (vs, sp) from asymmetric stretching vibrations of the Si$_8$O$_{12}$ cage and 750 (m, sp) from Si-C stretching vibrations.

Homopolymerisation of methacryl-POSS cage mixture (Exp. no. 99) was carried out following the same procedure as explained in section 4.2.3.3. After drying the product for 8 hours in a vacuum oven at 60°C, a yellow gel was obtained. This could be due to some methanol (solvent used to precipitate the polymer) entrapped within the network of the polymer. $^1$H NMR spectrum of the polymer (Figure 4.30) showed an intense peak at 3.49 ppm from methanol that was confirmed in a HMQC (Heteronuclear Multiple Quantum Coherence) experiment, where the carbon corresponding to this peak was at ca. 50 ppm (typical shift from C-OH). The estimate percentage conversion was 79 %, which is lower than in the case of poly(methacryl ethyl-POSS). It was thought that the bulkiness of the POSS cages could be largely responsible for this lower rate. It is important to mention that every methacryl-POSS cage monomer has 8 methacrylate branches, and it is very difficult to polymerise all of them because of the steric hindrance between 2 monomer molecules when they come close to each other.

![Figure 4.29. $^1$H NMR (CDCl$_3$) spectrum of methacryl-POSS cage mixture monomer.](image-url)
Figure 4.30. $^1$H NMR (CDCl$_3$) spectrum of poly(methacryl-POSS cage mixture) after 86 hours of polymerisation.

The presence of unreacted methacrylate functionalities in the product was confirmed by DSC, where a large exotherm due to further polymerisation of these unreacted methacrylate groups was observed in the first scan of the product. During the second scan no exotherm was seen, because as a consequence of heating during the first scan, all the methacrylate groups were already reacted (Figure 4.31).

Figure 4.31. DSC analysis of exp. no. 99 product, poly(methacryl-POSS cage mixture).

The FT-IR spectrum of poly(methacryl-POSS cage mixture) (exp. no. 99) showed absorptions at $v_{max.}$ (cm$^{-1}$): 2963-2883 (m, b) from C-H stretching vibrations; 1722 (m, sp)
from C-O vibrations; 1460 (w, sp) from C-H bending vibrations; 1253 (m, sp) from Si-Et symmetric deformations; 1072 (vs, sp) from asymmetric stretching vibrations of the Si₈O₁₂ cage and 758 (m, sp) from Si-C stretching vibrations.

4.3.2.2 Co-polymerisation of POSS reagents with MMA at 85°C.
Methacryl ethyl-POSS and methacryl-POSS cage mixture have the methacrylate functionality in common, so it was thought that polymerisation could take place easily between these reagents and MMA (Figure 4.32).

![Figure 4.32. Scheme of copolymerisation of methacryl ethyl-POSS with MMA (I) and methacryl-POSS cage mixture with MMA (II).](image)

Methacryl ethyl-POSS (monofunctional) would form a pendant polymer structure and methacryl-POSS cage mixture (8 methacrylate groups) would lead to a crosslinked polymer structure (Figure 4.33) upon co-polymerisation.

![Figure 4.33. Possible structure of copolymers formed with POSS reagents and MMA.](image)

In the first approach, a 1:1 molar ratio (POSS monomer: MMA) was investigated in a typical emulsion polymerisation process (procedure explained in section 4.2.3.4). SDS was used as stabiliser system and potassium persulfate was used as initiator of the free
radical polymerisation process. Both experiments were maintained at 85°C for 86 hours. The results for both experiments are detailed in Table 4.3.

**Table 4.3. Results of co-polymerisation of POSS monomers and MMA at a 1:1 molar ratio.**

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Co-monomers</th>
<th>Product</th>
<th>IR absorptions (cm⁻¹) (approximate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>Methacryl ethyl-POSS (1.87 g, 2.5 mmol) + MMA (0.25 g, 2.5 mmol)</td>
<td>2.01 g (95 %) white powder</td>
<td>2968-2880 (m, b); 1722 (s, sp); 1461 (m, sp); 1253 (m, sp); 1080 (vs, sp); 758 (m, sp) and 693 (s, sp)</td>
</tr>
<tr>
<td>101</td>
<td>Methacryl-POSS cage (3.58 g, 2.5 mmol) + MMA (0.25 g, 2.5 mmol)</td>
<td>3.68 g (96 %) white powder</td>
<td>2946-2850 (m, b); 1725 (s, sp); 1460 (m, b); 1252 (m, b); 1088 (vs, sp); 748 (m, b) and 688 (m, b)</td>
</tr>
</tbody>
</table>

Despite the high yields obtained, not all the material recovered was polymer. Unreacted monomer was found to be present in both products, as can be seen in the ¹H NMR spectra of the polymers (Figures 4.34 and 4.35).

**Figure 4.34.** ¹H NMR (CDCl₃) spectrum of co-polymer methacryl ethyl-POSS + MMA (1:1 molar ratio) (Exp. no. 100).

In the case of the co-polymer methacryl ethyl-POSS + MMA, the relative intensities of the peaks from the methacrylate backbone of the polymer (a and d in Figure 4.34) are relatively small in comparison with the peaks corresponding to the unreacted monomer (both protons from the double bond and methyl protons from CH₃-C=C which typically appears at 1.9 ppm). Thus, it was deduced that the polymerisation was incomplete and slow probably due to the steric hindrance caused by the large cages of Si₈O₁₂ (the estimate percentage conversion was 79 %). DSC analysis of the product obtained showed an exotherm during the first scan due to further reaction of unreacted methacryl groups.
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when heat was applied to the sample. Thus, the presence of unreacted methacrylate groups within the product was confirmed.

![Figure 4.35. $^1$H NMR (CDCl$_3$) spectrum of co-polymer methacryl-POSS cage mixture + MMA (1:1 molar ratio) (Exp. no. 101).](image)

As mentioned above (exp. no. 100), the $^1$H NMR spectrum of the co-polymer formed by methacryl-POSS cage and MMA (Figure 4.35) showed peaks from unreacted monomer. The estimate percentage conversion was 72%. The presence of unreacted methacrylate groups was confirmed by the exotherm obtained during DSC analysis of the product.

4.3.2.3 Homopolymerisation of POSS reagents at 60°C.

Emulsion homopolymerisation systems under different conditions than before (section 4.3.2.1) were investigated here, such as different polymerisation temperature and different solvent for precipitation of the polymer from the latex.

In free radical polymerisation systems, when the temperature is very high, the initiator undergoes thermolysis very quickly, and subsequently, the initiator concentration would be high. As a consequence of the high temperature and the consequently high initiator concentration, the number of oligomers is high. These oligomers are thus more statistically likely to react with another oligomer and terminate the reaction at the beginning of the process leading to short chains of polymer$^{46}$. Decreasing the temperature to 60°C, the initiator undergoes thermal degradation more gradually, thus the initiator concentration would be lowered, leading to longer polymer chains.
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In previous experiments, relatively intense $^1$H NMR signals for CH=C were observed because there was still some unreacted POSS monomer in the product. Thus, the solvent used to precipitate the polymer (methanol), was also precipitating the monomer. It is known that both POSS monomers used here are soluble in acetone, whilst typical PMMA systems are insoluble in acetone. Therefore, it was thought that using acetone to precipitate the polymer would be a successful method to avoid having unreacted monomer present within the product.

Apart from the two variations mentioned above (reaction temperature at 60°C and using acetone to precipitate the polymer), homopolymerisations of methacryl ethyl-POSS (Exp. no. 102) and methacryl-POSS cage mixture (Exp. no. 103) were carried out as described in section 4.2.3.3 (the reaction time was increased to 5 days). Table 4.4 summarises the results obtained for both homopolymerisations.

Table 4.4. Results of homopolymerisation of POSS reagents at 60°C.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Monomer Product</th>
<th>$^1$H-NMR (ppm) (CDCl$_3$)</th>
<th>IR absorptions (cm$^{-1}$) (approximate)</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>Methacryl ethyl-POSS (3.74 g, 5 mmol) 3.40 g (91 %) tacky gel</td>
<td>4.12 (t, 2 H); 1.71 (m, 2 H); 1.26 (m, 2 H); 0.98 (t, 3 H); 0.87 (m, 3 H); 0.60 (m, 2 H)</td>
<td>2962-2856 (m, b); 1732 (w, sp); 1460 (w, sp); 1253 (m, sp); 1082 (vs, sp); 695 (m, sp)</td>
<td>1st analysis: C, 65.3; H, 11.2 %</td>
</tr>
<tr>
<td>103</td>
<td>Methacryl-POSS cage mixture (7.16 g, 5 mmol) 4.59 g (64 %) white powder</td>
<td>4.10 (t, 2 H); 1.75 (m, 2 H); 1.25 (m, 2 H); 0.88 (m, 3 H); 0.66 (m, 2 H)</td>
<td>2955 (w, b); 1716 (s, sp); 1638 (w, sp); 1452 (w, b); 1263 (w, b); 1088 (vs, sp); 695 (m, sp)</td>
<td>1st analysis: C, 43.5; H, 6.24 %</td>
</tr>
</tbody>
</table>

The product of exp. no. 102, poly(methacryl ethyl-POSS), showed typical peaks of the methacrylate backbone in $^1$H NMR spectroscopy (1.26 ppm and 0.87 ppm). It was isolated as a tacky gel, which could mean that there was some acetone, used for precipitating the polymer, entrapped within the pendant polymer. As a consequence of that, elemental analysis was in great disagreement with the theoretical value (Table 4.4). Therefore, the product yielded (3.40 g) was not wholly polymer, as it included a large amount of acetone, which could be observed in the $^1$H NMR spectrum at 2.17 ppm. It
was thought that molecules of acetone (polar solvent) could be entrapped in the cages of
the pendant polymer, leading to a tacky gel as product even after drying it under vacuum
at 60°C for 10 hours.

DSC analysis of the product showed a small exotherm in comparison with previous
experiments (Figure 4.36). This could mean that there were not many unreacted
methacrylate groups within the product. This is confirmed by ¹H NMR spectroscopy as
no CH=C signal was observed. Therefore, the temperature and reaction time used during
this experiment (Exp. no. 102) seem to be good conditions for the formation of the
pendant poly(methacryl ethyl-POSS).

On the other hand, homopolymerisation of methacryl-POSS cage mixture (Exp. no. 103)
lead to a white powder. ¹H NMR spectroscopy showed typical methacrylate backbone
peaks. The results of elemental analysis were in good agreement with theoretical values
(Table 4.4). DSC experiments showed an exotherm during the first scan of the sample
probably because of the presence of some methacrylate groups in the product (Figure
4.37). This could be due to the presence of 8 methacrylate groups per Si₈O₁₂ cage, and
even though polymerisation occurred (methacrylate backbone ¹H NMR signals were

Figure 4.36. DSC analysis of poly(methacryl ethyl-POSS) formed using 60°C and 5 days as
polymerisation conditions (Exp. no. 102).
observed), it is very difficult to react all the substituents of such a bulky moiety as the Si$_8$O$_{12}$ cages.

![Figure 4.37. DSC analysis of poly(methacryl-POSS cage mixture) formed at 60°C for 5 days as polymerisation conditions (Exp. no. 103).](image)

4.3.2.4 Co-polymerisation of POSS reagents with MMA at 60°C.

POSS reagents were co-polymerised with MMA as in section 4.3.2.2 with a difference in the molar ratio of POSS monomer to MMA. Previously, a molar ratio of 1:1 led to a situation with high steric hindrance because of the bulkiness of the POSS cages. Therefore, using a higher ratio of MMA co-monomer, there would be longer methacrylate chains between cages, facilitating the addition of bulky monomers. A molar ratio of 1:5 (POSS monomer: MMA) was investigated. The same procedure as explained in section 4.3.2.3 was followed with reaction time increased to 8 days. The results obtained are summarised in Table 4.5.
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Table 4.5. Results of co-polymerisation of POSS monomers with MMA at a 1:5 molar ratio.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Co-monomers</th>
<th>Product</th>
<th>IR absorptions (cm⁻¹) (approximate)</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>104</td>
<td>Methacryl ethyl-POSS (1.87 g, 2.5 mmol) + MMA (1.25 g, 12.5 mmol)</td>
<td>2.13 g (68%) tacky gel</td>
<td>2960-2855 (m, b); 1732 (m, sp); 1460 (m, sp); 1253 (m, sp); 1085 (vs; sp); 695 (m, sp); 615 (m, sp)</td>
<td>1st analysis: C, 58.1; H, 10.4 %  2nd analysis: C, 57.5; H, 10.1 % (calc.: C, 44.3; H, 6.90)</td>
</tr>
<tr>
<td>105</td>
<td>Methacryl-POSS cage (3.58 g, 2.5 mmol) + MMA (1.25 g, 12.5 mmol)</td>
<td>2.76 (57%) white powder</td>
<td>2954-2870 (m, b); 1717 (s, sp); 1452 (m, b); 1260 (m, sp); 1076 (vs, sp); 695 (m, sp)</td>
<td>1st analysis: C, 39.2; H, 6.06 %  2nd analysis: C, 38.6; H, 6.11 % (calc.: C, 50.3; H, 6.62)</td>
</tr>
</tbody>
</table>

Co-polymerisation of methacryl ethyl-POSS with MMA in a molar ratio 1:5 (Exp. no. 104) yielded a tacky gel, which could be due to the presence of some acetone within the final product (typical acetone ¹H NMR signal was observed at 2.17 ppm, Figure 4.38 left). The presence of acetone within the product could explain the elemental analysis figures being higher than the theoretical values (Table 4.5). The absence of the ¹H NMR signals for CH=C together with the absence of an exotherm in DSC analysis lead to the conclusion that no unreacted monomer was presence in the final product.

The co-polymer produced in exp. no. 105 (methacryl-POSS cage + MMA) yielded a white product (Table 4.5). When precipitating the polymer in acetone, the monomer dissolved in this solvent, so unreacted monomer was not expected within the product. Elemental analysis figures showed lower values than the theoretical ones (Table 4.5). During polymerisation, the theoretical ratio was 1:5, but it may be that for every molecule of POSS monomer, more than 5 molecules of MMA reacted with the monomer, leading to a random ratio (higher than 1:5). The theoretical figures in elemental analysis were calculated for a 1:5 ratio, but because the unreacted monomer was dissolved in acetone, the proportion of POSS monomer in the copolymer could be lower and MMA higher, leading to lower percentages in C and H as expected. An exotherm was observed in DSC analysis because of the presence of unreacted methacrylate branches around the Si₈O₁₂ cages of the polymer. Due to these bulky Si₈O₁₂ cages, it is very difficult for every single methacrylate group to undergo polymerisation, and this is why the exotherm was observed in DSC analysis. Due to the heat from the first scan, these unreacted groups underwent further polymerisation, leading to an exotherm in the DSC plot.
However, the formation of the co-polymer chain was confirmed in both experiments (104 and 105) in the $^1$H NMR spectra (Figure 4.38), where typical signals for the methacrylate backbone were observed (a and b in Figure 4.38).

Figure 4.38. Left: $^1$H NMR (CDCl$_3$) spectrum of co-polymer methacryl ethyl-POSS + MMA (1:5 molar ratio) (Exp. no. 104). Right: $^1$H NMR (CDCl$_3$) spectrum of co-polymer methacryl-POSS cage mixture + MMA (1:5 molar ratio) (Exp. no. 105).

TEM images of copolymers were taken to investigate the morphology of the latex particles. A few drops of the latices from both co-polymerisations (experiments 104 and 105) were deposited on Cu grids and left to dry at room temperature for two days. The pictures obtained are shown in Figures 4.39 and 4.40.

Figure 4.39. TEM images of POSS + MMA co-polymers in molar ratio of 1:5 (left: methacryl ethyl-POSS + MMA, exp. no. 104; right: methacryl-POSS cage + MMA, exp. no. 105).

Spherical particles were observed in both latices (Figure 4.39). In the case of the co-polymer formed by methacryl ethyl-POSS and MMA (1:5 molar ratio, exp no. 104),
spherical particles with a regular diameter of ca. 10-15 nm were obtained (Figure 4.39, left). Co-polymer formed by methacryl-POSS cage and MMA (1:5 molar ratio, exp. no. 105) presented two sizes of spherical particles: ca. 15 nm and ca. 5 nm, which appeared very well dispersed in the latex (Figure 4.39, right).

Further TEM studies of the latices of these co-polymers lead to surprising structures of the co-polymer formed by methacryl ethyl-POSS + MMA (Exp. no. 104). Dendritic structures were found in different areas of the grid in TEM analysis (Figure 4.40).

Figure 4.40. TEM pictures of co-polymer formed by methacryl ether-POSS + MMA in a molar ratio of 1:5 (Exp. no. 104).

The structures showed in Figure 4.40 represent droplets where polymer particles are aggregated in a 'string of pearls' type structure leading to a dendritic structure. These droplets are surrounded by molecules of surfactant giving stability to the system in the aqueous media.

4.4 Conclusions

A free-radical emulsion polymerisation system was investigated for the synthesis of PMMA nanoparticles of ca. 50 nm in diameter. The morphology of the products obtained was analysed using SEM and TEM, and spherical nanoparticles were found under the following conditions: emulsion system with MMA as monomer, SDS as surfactant (2 % m.w.) and potassium persulfate as initiator (1 % m.w.); monomer and surfactant were
dispersed using ultrasound for an hour under nitrogen. The initiator was then added and the system was vigorously stirred (mechanical stirrer) for 6 hours at 60°C.

POSS reagents have been reported to be used in different polymerisation methods, but as far as we know, this is the first time that polymers containing methacrylate functionalised POSS reagents have been produced using free-radical emulsion polymerisation techniques. Two different POSS-methacrylate monomers have been homopolymerised and co-polymerised with MMA in different molar ratios.

POSS methacrylate monomers have been homopolymerised under certain conditions (5 days at 60°C) leading to two different polymers structures depending on the monomer used. Monomethacrylate POSS monomer led to a pendant polymer whilst octamethacrylate POSS monomer polymerised to give a crosslinked structure.

When methacryl ethyl-POSS (1 methacrylate branch and 7 ethyl groups around the Si₈O₁₂ cage) was co-polymerised with MMA (1:5 molar ratio), spherical nanoparticles of ca. 10-15 nm in diameter were observed by TEM. Some of these spherical nanoparticles were very well dispersed, but some others were aggregated following a ‘string of pearls’ type structure.

Co-polymerisation of methacryl-POSS cage monomer (8 methacrylate branches around the Si₈O₁₂ cage) with MMA (1:5 molar ratio) lead to spherical nanoparticles ranging from ca. 5 to 15 nm in diameter (the typical POSS macromer containing cyclohexyl groups is approximately 14 Å in diameter).

In all cases, polymerisation was confirmed by the typical ¹H NMR signals of the methacrylate backbone in the area of 0.7-1.3 ppm, although traces of unreacted monomer were also present in the majority of experiments.
4.5 References.

Chapter 4: Emulsion Polymerisation of Polyhedral Oligomeric Silsesquioxanes


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Chapter 4: *Emulsion Polymerisation of Polyhedral Oligomeric Silsesquioxanes*


Chapter 5

Conclusions and Future Work
5.1 Summary and Conclusions.
The non-hydrolytic sol-gel process has been successfully used for the synthesis of ormosils. The effect on morphology of the ormosil particles has been investigated using different solvents, types of stirring, and additives such as surfactants or polystyrene. The products were organic-inorganic hybrid (nano)composite materials where the organic modifications are covalently attached to silicon. The ormosils produced were characterised by IR spectroscopy, $^{29}$Si NMR spectroscopy, elemental analysis and SEM.

For the first time, some control over the product morphology during the non-hydrolytic sol-gel synthesis of ormosils has been achieved. This morphology control was one of the goals of this project. The use of solvents in which the precursors are soluble led to spherical ormosil particles, where the inorganic content of the hybrid (silica network) forms the core of the particles and the organic groups surround the inorganic oxide interacting with the non-polar solvent.

To evaluate the effect of the organic content on the morphology of the resulting ormosil, four different organic groups (methyl, ethyl, hexyl and phenyl) were introduced into the hybrid. The type of organic substituent used was observed to be an important factor in the structure of the hybrid, because spherical particles were obtained using methyl substituents under certain conditions (using Brij® 52 as surfactant or using DMSO as oxygen donor), whilst under the same conditions, ethyl-modified silicate particles were found to have irregular shapes.

Chapter 2 detailed the optimisation of the non-hydrolytic sol-gel process conditions in order to try to produce spherical particles with low level of aggregation. Different process parameters were investigated and they are described below.

The use of different solvents as the inert dispersing medium allowed some control over the product morphology. The solvent was selected to dissolve the catalyst of the reaction, iron(III) chloride, and to homogenise the commercially available precursors, TEOS and a variety of alkyltrichlorosilanes. They were soluble at the start of the reaction and the
product precipitated out as the reaction progressed. Thus, the process behaved like a dispersion polymerisation. A mixture of toluene and petroleum ether (boiling range of 100-120°C) in a proportion of 25:75 in volume was found to be the most effective in reducing the aggregation of the smallest particles. The relative proportions of the two solvents were found to influence the degree of aggregation of the smallest particles (as the solvent was richer in petroleum ether, the aggregation diminished).

As has been mentioned above, the synthesis of ormosil particles by the non-hydrolytic sol-gel route goes through a 'pseudo-dispersion' polymerisation process. Therefore, the morphology of the particles formed was strongly influenced by the degree of phase dispersion. An overhead mechanical stirrer was used during the most part of the work, and a decrease in the particle size was achieved upon the use of a high speed stirrer (Ultra Turrax®).

Surfactants were used during the polymerisation process to stabilise the hybrid particles whose components have totally opposite polarities (organic content and silica network). A range of five non-ionic polyoxyethylene ethers with different polarities was used to control the aggregation of the smallest particles during the polymerisation process. The least polar of the surfactants (polyoxyethylene 2-cetyl ether, Brij® 52) was found to be the most effective, achieving spherical ormosil particles in the size range 100 nm-1μm. These spherical shaped particles were one of the main targets of this work.

The use of polystyrene as an additive to the system to increase the viscosity of the reacting medium was investigated. Different amounts of polystyrene of different molecular weights were used, leading to the conclusion that very viscous solutions (20% of polystyrene of Mn ca. 45,000 based on the amount of solvent used) were needed to achieve spherical ormosil particles with relatively low aggregation. The polymer chains of polystyrene interacted with the colloidal solution interfering with the aggregation of the smallest particles.
Chapter 5: Conclusions and Future Work

DMSO was investigated as both a novel oxygen donor and solvent in a non-hydrolytic sol-gel process which occurred in the absence of any catalyst. The products of these reactions were silsesquioxanes where every silicon atom is attached to an organic substituent. Spherical particles of ca. 1 µm in diameter were observed in the methyl-modified silsesquioxane structure. An advantage of this novel route is the absence of any contamination from the catalyst, leading to white powders which could be useful for future applications (the use of FeCl₃ in the previous route produced discoloration of the otherwise colourless ormosils).

Chapter 3 reported the use of selected ormosils from Chapter 2 as additives to an epoxy resin system (XLVR16-2 epoxy resin) which is liquid at room temperature. The resin investigated is a trifunctional system (triglycidyl-β-aminophenol), thus, when cured, a three-dimensional network with high crosslink density is formed. Highly crosslinked epoxy resins are known as brittle thermosetting polymers which need to be toughened for various applications. Some of the ormosils produced in Chapter 2 were investigated as toughening agents.

Hybrid particles were blended into the epoxy resin using a mechanical stirrer. The epoxy resin maintained its excellent handling conditions upon modification with the hybrids, because the viscosity of the filled systems did not increased significantly. This is an important feature of these filled epoxy resins for future uses in resin injection techniques.

The fracture surface studies of the cured systems showed that the ormosil particles from the non-hydrolytic sol-gel condensation of TEOS with alkyltrichlorosilanes did not aggregate together during the blending process. These ormosil additives were uniformly dispersed throughout the resin matrix because of the good compatibility of their structure with the epoxy resin backbone. When using a non-polar solvent (such as one with long alkyl chains) for the synthesis of ormosils, the organic content projects into the solvent, and the inorganic material forms the nucleus of the hybrid particles. As a result of this distribution, good compatibility between both components (ormosil and epoxy resin) was found. Hence, ormosil particles were well dispersed within the epoxy resin matrix.
Chapter 5: Conclusions and Future Work

Another factor increasing the compatibility of the ormosil-epoxy system was that in the non-hydrolytic sol-gel route to ormosils, $Q^3$ and $T^2$ species were obtained as the polymerisation reaction did not proceed to completion. The unreacted alkoxy groups of the oligomers could improve the epoxy-ormosil compatibility, with a potential grafting to the epoxy resin matrix. As a result of the possible reaction, the dispersion of the ormosil within the epoxy resin matrix would be improved.

However, when producing silsesquioxanes using a polar solvent (such as DMSO) a different hybrid structure was proposed. Whilst the inorganic content of the hybrid was thought to be projecting into the solvent, the organic content was forming the core of the particles. Thus, compatibility of hybrid-epoxy resin was decreased, leading to phase separation when blending silsesquioxanes synthesised using DMSO with the epoxy resin system.

Final products were characterised by techniques such as fracture toughness testing, DSC, DMTA and SEM. Upon the use of ormosils as additives, some mechanical properties of the epoxy resin were improved (fracture toughness), but some thermal properties were lowered (decrease in $T_g$). Therefore, to enhance the mechanical properties without sacrificing the thermal ones, the filler size and concentration have to be carefully chosen. The biggest improvement in the fracture toughness (50 % greater than that of the unmodified resin) was produced using 5 phr of ethyl-modified silicate as additive. Thus, one of the main aims of the project, to improve some mechanical properties of epoxy systems using ormosils as additives, was achieved.

DMTA and DSC analyses revealed a decrease in the glass transition temperatures of the resin when increasing the ormosil concentration as additive, which might be due to the plasticising effect of the ormosil particles in the epoxy network, resulting in a lowering of the crosslink density. Despite this decrease, the $T_g$ of the filled epoxy resin systems was still high (ca. 200-210°C).
Chapter 5: Conclusions and Future Work

The effect produced by the hybrid over the final properties of the filled resin was varied changing the nature of the organic groups from none, methyl, ethyl, hexyl to phenyl. Methyl-modified silicates were found to be the fillers that showed the lowest decrease in the $T_g$ of the system. When ormosils with larger organic groups were investigated, a bigger decrease in the $T_g$ was found. This could be due to greater plasticising effect when the size of the organic moiety is increased. Thus, the crosslink density of the resin was lowered with the increase in the size of the organic group of the ormosil. The amount of filler added was also found to be an important factor in the $T_g$ of the resin. The higher the concentration of ormosil, the larger the plasticising effect observed, as was expected. Therefore, the effect of different organic groups in the ormosils on the final properties of the filled epoxy resin was evaluated.

Chapter 4 describes the optimisation of the free radical emulsion polymerisation conditions for the formation of PMMA spherical particles of ca. 50 nm in diameter. The conditions were then applied to the polymerisation of POSS-methacrylate monomers. Two kinds of polymerisations were investigated: homopolymerisation of two types of POSS-methacrylate monomers (monosubstituted and octasubstituted) and copolymerisation of both POSS-methacrylate monomers with MMA in different molar ratios (1:1 and 1:5).

The products obtained were characterised by IR spectroscopy, $^1$H NMR spectroscopy, elemental analysis, DSC, SEM and TEM. In all cases, polymerisation was confirmed by the typical $^1$H NMR spectroscopy signals of the methacrylate backbone in the area of 0.7-1.3 ppm, although traces of unreacted monomer were also present in the majority of experiments.

POSS-methacrylate monomers have been homopolymerised (5 days at 60°C) leading to two different polymers structures depending on the monomer used. Homopolymerisation of methacryl ethyl-POSS (1 methacrylate branch and 7 ethyl groups around the Si$_8$O$_{12}$ cage) lead to a pendant polymer whilst methacryl-POSS cage monomer (8 methacrylate branches around the Si$_8$O$_{12}$ cage) polymerised in a crosslinked structure.
Chapter 5: Conclusions and Future Work

When methacryl ethyl-POSS was copolymerised with MMA (1:5 molar ratio), spherical nanoparticles of ca. 10-15 nm in diameter were observed in TEM microscopy. Some of these spherical nanoparticles were very well dispersed, but some others were aggregated in a ‘string of pearls’ type structure. Co-polymerisation of methacryl-POSS cage monomer with MMA (1:5 molar ratio) lead to spherical nanoparticles ranging from ca. 5 to 15 nm in diameter.

5.2 Future Work.

Many other experiments are suggested by this work but have not been attempted due to time constraints. Some of them are detailed below.

Viscosity measurements could be carried out on solutions where polystyrene is used to increase the viscosity during the non-hydrolytic sol-gel synthesis of ormosils.

In the synthesis of silsesquioxanes using DMSO as oxygen donor and solvent, a $^1$H NMR spectrum could be carried out to confirm the presence of CH$_3$-S-CH$_2$Cl as by-product, and thus support the mechanism proposed in the discussion section of this work.

Measurements of the rheology of the ormosil-epoxy blends before and during curing could be of utility to further use of the blends in injection techniques.

Further characterisation of the epoxy resins modified with ormosils could be carried out using thermogravimetric analysis (measurement of the change of mass of the polymer sample as it is heated). Also water absorption of these systems could be measured, investigating if the different alkyl group in the ormosil would differently affect the water absorption of the filled systems.

As a consequence of toughening the epoxy resins using ormosils as additives, the crosslink density of the network was lowered. An investigation of a different cure cycle could be carried out to achieve a fully cured, filled epoxy resin system.
Chapter 5: Conclusions and Future Work

The silsesquioxanes produced by the DMSO route were not very compatible with the epoxy resin; a way to improve compatibility could be the use of a coupling agent such as 3-glycidoxypropyltrimethoxysilane (Figure 5.1) in the silsesquioxane-epoxy blend. The dispersion of the filler throughout the matrix could be investigated by XPS (X-ray Photoelectron Spectroscopy).

![Figure 5.1. Structure of 3-glycidoxypropyltrimethoxysilane (possible coupling agent to improve the compatibility of the silsesquioxane-epoxy blends).](image)

The emulsion copolymerisation of POSS-methacrylate monomers with MMA could be carried out with different molar ratios to the ones investigated here (e.g. 1:10 POSS: MMA). Also, a different kind of initiator could be investigated, such as an organic peroxide, to increase the reactivity of these systems.

POSS reagents are based on Si₈O₁₂ cages, which should have a great inherent porosity in the cube interiors. The formed polymers also have pores between the cages, and it would be interesting to measure these different types of pores using a surface analyser.

The hybrids obtained during the emulsion polymerisation of POSS reagents could be used as toughening agents for the epoxy resin system described before. Thus, a comparison of the effects produced with both types of hybrids (POSS polymers and ormosils) could be made.