Structure-property relationships of rubber/silica nanocomposites via sol-gel reaction

PROEFSCHRIFT

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Za mojata Majka i Baba...
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Summary

Up to date conventional mixing of rubber with silica is a time and energy consuming process where silica aggregates are dispersed throughout the rubber matrix. A way to avoid silica aggregation and to improve dispersion is to grow silica particles directly into the rubber matrix using the sol-gel chemistry. This idea triggered a PhD project where the main goal is to gain a clear understanding about the structure, the formation mechanism and the resulting properties of in-situ prepared rubber/silica nanocomposites. The gained knowledge will be then used to obtain in-situ nanocomposites via a reactive extrusion process.

In Chapter 1 of the thesis the current state of art in the field of nanocomposites is given, with emphasis on the preparation and properties of nanocomposites produced via sol-gel reaction. Outlined are also the objectives of the study to provide deep understanding of the mechanism and the kinetics of the sol-gel reaction in rubber matrix and to correlate the structure of the in-situ synthesized silica to the properties of the nanocomposites.

Rubber/silica nanocomposites were prepared via sol-gel reaction, using TEOS as precursor and hexylamine as catalyst. The effect of different reaction parameters—amount of precursor, reaction time, temperature and type of rubber on the morphology of the prepared in-situ nanocomposites (loading, size and dispersion of silica) is shown in Chapter 2. The TEM images of the nanocomposites indicated excellent dispersion of the silica particles. The amount of the bound rubber was evaluated and correlated to the rubber-silica interaction.

The kinetics and the mechanism of the sol-gel reaction in a rubber matrix were studied in detail by performing time-resolved solid-state NMR and SAXS experiments. The results presented in Chapter 3 indicate that the sol-gel process in rubber matrix adopts the emulsification process behaviour, where hexylamine, used as catalyst, behaves as surfactant forming inverse micelles with enclosed water in TEOS-swollen rubber matrix. The growth of the silica particles with time was probed via SAXS and a comparison is made between the growth rate of different type of rubbers and at different temperatures.
The structural investigation of the in-situ synthesized silica particles, presented in Chapter 4, was performed using solid state NMR and MS-TGA-IR. For the first time we show that via the sol-gel process so called ‘hairy’ silica particles are formed, with hexylamine and remnant ethoxy groups residing predominantly on the silica surface. This “hairy” silica surface resulted in a more hydrophobic nature of the silica particles and thus to improved rubber-silica interaction.

In Chapter 5 the properties of the in-situ nanocomposites produced in both-static and dynamic conditions (batch mixer) are discussed and compared to those of the conventionally prepared rubber/silica nanocomposites. The RPA measurements of the in-situ nanocomposites indicated a strong reinforcement effect, at much lower silica loadings in comparison to the conventional rubber/silica nanocomposites. We explain this strong reinforcement in the in-situ prepared rubber/silica nanocomposites with the improved rubber-silica interactions (caused by the specific surface topology of the in-situ silica) and by the presence of trapped entanglements and bound rubber. The in-situ rubber/silica nanocomposites were successfully produced also via reactive extrusion, which was one of the targets of the thesis. As shown in Chapter 5, the nanocomposite obtained in this way with maximum loading of 3.2 wt% silica, possessed a uniform dispersion of the silica particles and very good properties. Chapter 6 contains the technological assessment of this study. The importance and the possibilities for industrial application of the sol-gel process to obtain rubber-silica nanocomposites with excellent properties are discussed.
Silica is used as reinforcing filler in the rubber industry for preparation of the rubber/silica nanocomposites. The preparation of these materials requires several mixing steps to disperse the silica aggregates throughout the rubber matrix. An alternative approach is the sol-gel process for silica formation. The sol-gel reaction allows growth of the silica particles directly into the rubber matrix, possibly with a different surface chemistry. It is believed to result in improved rubber-silica interactions and thus improved mechanical properties of the obtained rubber/silica nanocomposites.
1.1. **Polymers**

Polymers are long-chain molecules composed of chemically linked building blocks, called monomers. Polymers show visco-elastic properties and have the possibility to exhibit rubbery-like behaviour above their glass transition temperature \( T_g \). The \( T_g \) is determined by the chemical structure of the polymer, chain flexibility and the inter-chain interactions. Based on their chemical structure and thermal behaviour polymers can be divided into three main classes, namely thermoplastics (amorphous and crystalline), rubbers and thermosets. The difference in the mechanical properties with temperature of these materials is shown in Figure 1.1.

![Thermo-mechanical curves behaviour of amorphous, crystalline and rubber (crosslinked and non-crosslinked) materials.](image)

It is noted that thermosets are not included in Figure 1.1. The reason is that they possess very high \( T_g \), close or in some cases equal to the degradation temperature thus resulting in very small changes of the mechanical properties with temperature. The thermal behaviour of polymers is divided into three regions, i.e. the glassy region below \( T_g \), the rubbery region above \( T_g \) and the flow region at higher temperatures. Each of these regions is related to specific types of molecular motions of the polymer chain as the temperature increases and is characteristic for
each class of polymers depending on their chemical structure, thus the $T_g$ of the material. Above $T_g$ amorphous polymers are in the ‘rubbery’ state with usually $T_g$ being their limiting application temperature, while crystalline polymers above $T_g$ are in the so-called ‘flexible-crystalline’ state with the melting temperature ($T_m$) as their limiting application temperature.\textsuperscript{1,2} In general, rubbers have flexible, long chain molecules and glass transition temperatures ($T_g$) below room temperature. They can exist in two states, as non-crosslinked and crosslinked. In Figure 1 the non-crosslinked rubber shortly after reaching $T_g$ starts to flow, while the crosslinked rubber due to the presence of chemical bonds has limited possibility to flow and it maintains a rubbery plateau at higher temperatures until it eventually degrades. Interestingly, the modulus of the crosslinked rubber slightly increases with temperature which can be explained by the following equation:

$$E = \frac{3\rho RT}{M_c}$$  \hspace{1cm} (1.1)

where, $\rho$ - density of rubber, $R$ - gas constant, $T$ - temperature and $M_c$ - the molecular weight between crosslinks.

Cross-linking is a method during which chemical bonds are formed between the polymer chains. The two main cross-linking techniques for rubber are sulphur vulcanization and peroxide curing.\textsuperscript{3,4} Charles Goodyear discovered the sulphur vulcanization in 1839 opening many new applications for rubber materials. It is believed that he discovered the effect by accidental dropping a mixture of rubber and sulphur on a hot stove where instead of melting, the mixture turned into a hard vulcanized material. Sulphur vulcanization is limited to rubbers with un-saturation, while the peroxide method can be performed even on rubbers that do not possess un-saturations. Rubber crosslinking results in the formation of a 3D network of polymer chains connected by sulphur bridges in sulphur vulcanization and by C-C bonds in peroxide curing.\textsuperscript{1,5}

According to the ASTM D1566 standards rubber is defined as a material that can be extended to twice its original length ($2L_0$) and when released it can recover to less than 1.5 $L_0$ within 1 minute at room temperature. It is crosslinked and cannot
be dissolved in a boiling solvent, but can swell. In the following chapters of this thesis the term rubber will be used for all non-crosslinked polymers (natural rubber (NR), ethylene-propylene diene monomer (EPDM) and styrene-butadiene rubber (SBR)) that fulfil the requirements to be rubber (low $T_g$, amorphous, flexible chains). Only when these polymers are crosslinked the term crosslinked rubber will be additionally used to emphasize that the rubber is crosslinked. Therefore, in this thesis the rubber is a polymer which has only physical cross-links between the chains that upon stress begin to disentangle leading to a permanent deformation with no possibility, upon release of stress, to retract back to its initial state, thus limited elastic properties. It has no solvent resistance and exhibits very low mechanical properties. The cross-linked rubber has permanent chemical cross-links between the chains that gives the material dimensional stability and higher stiffness. The crosslinked rubber possesses elastic properties which means that it can be stretched substantially beyond its original length and retract rapidly to its almost original dimensions.\textsuperscript{4}

In general both, natural and synthetic sources can be used to produce rubbers. The first material known as rubber is obtained in the form of latex from the tree Hevea Braziliensis and is called natural rubber (NR). The NR latex is known since the year 1500, when it was used in the Inca civilization for making water proofed clothing, shoe soles and rubber balls for a ball game. The word rubber comes from the ability of this material to rub off pencil marks from paper as observed by Priestley in 1770.\textsuperscript{6} The first attempts for the production of synthetic rubber on commercial scale (methyl rubber) were initiated by Germany, due to lack of NR during the First World War. During the Second World War, due to shortage of NR, two synthetic types of rubber butadiene and styrene-butadiene rubber were produced in USA and Germany. In the 1950/60’s other synthetic rubbers were developed, with EPDM becoming the most important non-tire rubber.\textsuperscript{3}

1.1.1. Natural rubber (NR)

NR is collected from a tree in the form of latex, an emulsion of small rubber
particles with sizes in the range of 0.1 - 1 µm in a watery liquid. The rubber content in the latex is 30 - 38 %. The rubber particles are stabilized with proteins residing on their surface and preventing them from coagulating. The chemical structure of NR consists of isoprene units which arrangement results in two different types of natural rubber, viz. the flexible cis - polyisoprene (Figure 1.2) and the more rigid trans - polyisoprene. The first one is the widely used natural rubber, the later is called gutta-percha and is hard material with a more thermoplastic behaviour.\textsuperscript{6,7}

![Chemical structure of isoprene in cis-configuration as building block in NR.](image)

NR is available in many commercial grades, depending on the polymer viscosity and the product purity. The non-rubber content (proteins, dust and other organic components) can vary and might significantly influence the price. Since the NR has tendency to harden upon storage, hydroxylamine salts are added for stabilization of the viscosity. Crosslinked NR has excellent mechanical and elastic properties which originate from the possibility to crystallize upon deformation and to obtain a high crosslink density upon vulcanization. The strain-induced crystallization of the NR is unique. It gives extra strength upon mechanical loading (Figure 1.3) and upon release of the stress, the NR snaps back to its initial state causing the formed crystallites during the deformation to disappear.
Figure 1.3. Tensile properties of NR (---) are superior to most synthetic rubbers (---) due to the strain-induced crystallization (low hysteresis) of NR.

The high network density gives good rebound properties and low hysteresis. NR has poor oil resistance and it is sensitive to ozone oxygen and UV radiation, due to its large amount of unsaturated bonds in the main chain. It has a good abrasion resistance that allows applications in slurry pump liners, impellers and tank linings and due to its good dynamic mechanical properties it is used in tires, rubber springs and vibration mounts. The low $T_g$ (-65 °C) provides good low temperature elasticity.\textsuperscript{2,3}

1.1.2. Ethylene-propylene copolymer (EPM) and ethylene-propylene-diene terpolymer (EPDM)

EPM is a copolymer of ethylene and propylene and can be cross-linked only by means of peroxides, due to the absence of unsaturation. On the other hand, EPDM (Figure 1.4) is a ter-polymer of ethylene and propylene with a diene monomer that provides residual unsaturation in the pendant side groups and allows crosslinking via sulphur vulcanization.
The properties of EPDM strongly depend on several characteristics such as ratio of the ethylene and propylene monomers, the distribution of these monomers in the main chain and the amount and type of the diene monomer. These structural parameters are determined by the catalyst structure and the polymerization conditions. The ethylene/propylene ratio in commercial products generally ranges from 45:55 to 80:20 (w/w). At higher propylene contents the thermal and oxidative stability of the polymer are negatively affected. At higher ethylene contents the polymer becomes too crystalline and loses its rubbery properties. Some crystallinity is beneficial because it gives EPDM a higher strength making the polymer easier to handle in the un-vulcanized state and better tensile properties in the crosslinked state. EPDM is synthesized mostly via solution polymerization using Ziegler-Natta catalysts which contain mainly vanadium compounds. It is a commercially attractive product, because it displays excellent heat, oxygen, and ozone resistance due to the low level of un-saturation (diene monomer content is only 4 - 8% present). On the other hand, the low content of un-saturation introduces certain disadvantages, such as a low crosslink density and slow vulcanization.

EPDM is mostly used for automotive sealing systems, roof membrane linings and extruded windows gaskets. It has an excellent electrical resistance and is used for the production of high voltage cable covers.

### 1.1.3. Styrene-butadiene rubber (SBR)

SBR was the most important rubber in the Second World War, when it was produced on a large scale in USA and Germany for the purpose of replacing NR in
tires. The possibility to vary the structure of SBR by changing the styrene and butadiene content during polymerization, offers great opportunities to construct tire treads with very good properties.\textsuperscript{3} SBR is a copolymer of styrene and butadiene (Figure 1.5).

Figure 1.5. Chemical structure of styrene-butadiene rubber (SBR).

The butadiene monomer provides flexibility, rubbery properties and unsaturation for the vulcanization reaction, while the styrene reduces the damping. Different SBR grades are obtained not only by varying the styrene/butadiene ratio, but also by the way the butadiene monomer (cis, trans or vinyl) configuration is incorporated in the chain. Thus, butadiene in the cis-configuration results in more flexible SBR, while the trans and vinyl configurations result in SBR grades with lower flexibility. The polymerization can proceed via emulsion and solution routes, resulting in two general types of SBR (emulsion and solution SBR). The emulsion polymerization involves emulsifiers, organic peroxides as initiator, stabilizers and coagulants in order to allow formation of less branched SBR. In emulsion polymerization the butadiene and styrene have equal tendency to add to the growing chain, forming highly random copolymers. The other polymerization route for SBR production is in solution using lithium-alkyls as catalysts in non-polar solvents. The SBR obtained via solution polymerization has a more blocky
copolymer structure with butadiene and styrene sequences randomly distributed throughout the chain. The reason for the block-like structure is the higher tendency of butadiene to add to the growing chain and it can even form a homopolymer instead of copolymer, if not controlled. Different polar substances like ethers and amines are added to promote more randomized polymerization.

Despite the efforts the structure of solution SBR always resembles more to a blocky copolymer. SBR exhibits a poorer crosslink network when compared to NR and as a result shows lower tensile strength and elasticity. SBR does not undergo strain-induced crystallization and requires much higher filler loadings for achieving good mechanical properties. In general, solution SBR is the cleaner grade with a narrower molecular weight distribution and less branching than emulsion SBR and is usually the preferred grade for the tire industry. It improves the skid resistance because of its poorer network and provides better heat and ozone resistance when compared to NR because of less un-saturation in the main chain.\textsuperscript{3,6} Other applications of SBR are in the area of belting, molded rubber goods, cable insulation and sealing’s.

\textbf{1.2. Fillers in rubber technology}

The crosslinked rubber materials have low mechanical properties and addition of fillers is necessary for achieving certain degree of reinforcement that leads to significant improvement of the mechanical properties. The reinforcement depends to a large extent on the polymer properties, filler characteristics (particle size or specific surface area, structure and surface activity), filler loading and processing conditions.\textsuperscript{9-11} In general, there are two types of fillers, non-active and active. This classification normally relates to the influence of the filler on the compound viscosity and on the mechanical properties of the final product, such as tensile strength, abrasion, tear resistance, hardness and elongation at break. The improved mechanical properties of the rubber nanocomposites are not solely based on the incorporation of hard fillers but also on the interactions developed between the filler and the matrix. These interactions can vary from strong (chemical bonds) to
intermediate (hydrogen bonding, dipole interactions) to weak (van der Waals). Well known active fillers, such as carbon black\textsuperscript{4,12} and silica\textsuperscript{13-15} have a greater influence on the physical properties of a rubber material than inactive fillers, like clay or calcium carbonate.\textsuperscript{16}

Moreover, the active fillers depending on their particle size can have reinforcing (0.01 - 0.1 µm), semi-reinforcing (0.1 - 1 µm) and non-reinforcing (1 - 10 µm) effect on the rubber material. The particle size is important because it represents the area available for interaction between the rubber and the filler, thus smaller size particles will have larger surface available for interacting with the rubber. Carbon black is one of the most exploited fillers in the rubber industry for more than hundred years already, particularly used for reinforcement of tires. In general, based on the production process we can distinguish three types of carbon black: furnace, channel and thermal, respectively. The furnace carbon black is by far the most important type, participating with 95% of the total amount of carbon black used in the rubber industry for production of tires. Different grades of carbon black are produced varying mainly in the size of the primary particle. Carbon black is widely used as black pigment for toners, as filler that provides electric conductivity and almost 70% of the total amount of carbon black is used in the tire industry. The application of the carbon black in the tire industry is predetermined by the reinforcing effect imparted to the rubber matrix, which in turn is strongly determined by the size of the primary particle where smaller size primary particles lead to higher reinforcement.\textsuperscript{3,17,32}

1.2.1. Silica as reinforcing filler

From the non-black fillers silica provides the highest reinforcement to rubber products which is ascribed to the small particle size of the silica. Silica is an amorphous material, consisting of silicon and oxygen atoms connected in a non-regular 3D network of Si-O-Si bonds with silanol groups (Si-OH) present inside and on the surface (Figure 1.6).\textsuperscript{18,19}
Figure 1.6. Structure of amorphous silica containing three types of silanol (Si-OH) groups.

Three different types of silanol groups can be distinguished on the silica surface: i) isolated silanol that has only one hydroxyl group, ii) vicinal that contains hydroxyl group’s close enough to develop hydrogen interactions and iii) geminal silanol where two hydroxyl groups are linked to one silicon atom. The silanol groups are directly responsible for the high polarity of the silica and the strong affinity to absorb water on its surface (~ 6% for precipitated silica). The silanol groups have a strong tendency to form hydrogen bonds with the silanol groups from the neighboring particles, resulting in aggregates with various sizes. Three structures of silica at different length scales are distinguished, such as primary particles (10 - 50 nm), aggregates (primary particles fused together via hydrogen bonding: 100 - 500 nm) and agglomerates (aggregates are held together with van der Waals forces: > 1 μm) (Figure 1.7).

Figure 1.7. Structural organization of primary silica particles into aggregates and agglomerates.
There are two types of commercially available silica: precipitated and fumed. The precipitated silica is prepared by the reaction of sodium silicate and sulphuric acid under alkaline conditions and the fumed silica is prepared by oxidation of silicon tetrachloride vapour at high temperatures (~ 1000 °C). The physical properties of these two amorphous silica grades are determined by the production route and the reaction parameters (Table 1.1). In the rubber industry the precipitated silica is the preferred type of silica used because of the lower price and better mixing with the rubber material. The more expensive fumed silica has very low bulk density (very fluffy white powder) due to which is mainly used in silicon rubber.

Table 1.1. Physical properties of amorphous silica

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<th>Property</th>
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<th>Fumed</th>
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<td>Surface area [m²/g]</td>
<td>60-300</td>
<td>50-400</td>
</tr>
<tr>
<td>Moisture [%]</td>
<td>&lt;6</td>
<td>&lt;1.5</td>
</tr>
<tr>
<td>Silanol groups [nm⁻²]</td>
<td>8-10</td>
<td>2-4</td>
</tr>
<tr>
<td>Primary particle size [nm]</td>
<td>10-50</td>
<td>7-50</td>
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</table>

Silica is also used in shoe soles for improving the resistance to wear and tearing. It is also used to improve the tear strength and heat aging resistance in a wide variety of manufactured rubber goods, including conveyor and power transmission belts, hoses, motor and dock mounts, bumper pads and rubber rolls. Nowadays, the application of rubber depends on finding the optimum balance between type and amount of filler needed for achieving maximum improvement in mechanical properties. Mixing of inorganic silica and organic rubber yields conventional rubber/silica nanocomposites with the silica dispersed in 10 - 100 nm range.

These nanocomposites are also called hybrid nanocomposites, because they combine the advantages of both materials: rigidity, thermal stability and barrier properties from the filler and flexibility, ductility and processability from the rubber.
1.3. Conventional rubber/silica nanocomposites

The process of producing rubber products is a complex process involving several production steps such as mixing or compounding, shaping and vulcanization. The mixing of the rubber material with other additives (silica, plasticizers/oil, coupling agent, vulcanization agents, antioxidants etc) is the crucial step, where an optimal balance between the rubber material and the additives must be achieved in order to meet the final product requirements.\textsuperscript{32} For conventional rubber/silica nanocomposites one of the challenges is to achieve good silica dispersion, required for achieving good mechanical properties of the rubber, which is difficult due to the high polarity of the silica and its strong tendency to aggregate.\textsuperscript{13,14,33}

The polarity of a material is characterized by the Hildebrand solubility parameter, as listed for several types of rubbers and fillers in Table 1.2. The solubility parameter can be used to predict the compatibility between the rubber and the filler, where closer values of the solubility parameters are expected to provide better compatibility, thus mixing. There is a large discrepancy between the solubility parameters of silica and the rubbers, indicating difficult mixing of these two materials. Insufficient mixing between these two materials usually results in large aggregates, non-uniformly dispersed throughout the matrix, leading to formation of rubber/silica nanocomposites with weak mechanical properties.\textsuperscript{13}

\textit{Table 1.2. Solubility parameters of rubbers and fillers.}\textsuperscript{34}

<table>
<thead>
<tr>
<th>Material</th>
<th>Hildebrand solubility parameter (MPa\textsuperscript{1/2})</th>
<th>PE: poly (ethylene)</th>
<th>EPM: ethylene-propylene rubber</th>
<th>EPDM: ethylene-propylene diene terpolymer</th>
<th>SRB: styrene-butadiene rubber</th>
<th>IIR: isobutylene isoprene rubber</th>
<th>NBR: Acrylonitrile -butadiene rubber</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE, EPM, EPDM</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR, BR, IIR</td>
<td>16-16.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBR</td>
<td>16.6-18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NBR</td>
<td>19-20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>28-36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon black</td>
<td>24-30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The mixing of rubber and silica is greatly improved by the addition of a coupling
agent.\textsuperscript{35,36} The role of the coupling agent is to chemically modify the silica surface by forming a hydrophobic layer, which allows easier breakage of the agglomerates into smaller aggregates during the mixing stage and their better dispersion in the rubber matrix. Additionally, coupling agents (bis (triethoxysilylpropyl) tetrasulphide - TESPT) have the ability to chemically bridge the silica surface and the rubber chains by forming sulphur bonds with the rubber and Si-O-Si bonds with the silica surface (Figure 1.8). Silica in combination with a coupling agent is superior when compared to carbon black because it provides a stronger reinforcing effect which allows the use of lower filler content in the rubber without any negative consequences on the mechanical properties. This additionally improves the elasticity of the rubber/silica nanocomposites resulting in reduction of the rolling resistance. Moreover, the chemical bonds between the silica and the rubber results in a more stable silica-rubber network that during cyclic deformation of the nanocomposite results in lower degree of breaking and reforming of the silica-rubber network. This results in lower loss modulus and consequently lower tan δ values which additionally reduces the rolling resistance.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{TESPT.png}
\caption{Schematic representation of silane coupling agent (e.g. TESPT) chemically bridging the silica surface and the rubber chain.}
\end{figure}

This behaviour of the rubber/silica nanocomposites enabled tire manufacturers to achieve simultaneous improvement in the three properties of the ‘Magic triangle’
i.e. skid resistance, abrasion and rolling resistance. The balance between the properties of the ‘Magic triangle’ is considered important and silica improves this balance.\textsuperscript{37,38}

There have been numerous efforts to improve silica dispersion, for example by varying the chemistry and content of the coupling agents, improving the mixer rotor design,\textsuperscript{14} ultrasound pre-treatment of the silica particles and different methods for chemical modification\textsuperscript{39-41} of the silica surface, but dispersion still remains a serious issue not only for rubber materials but also for thermoplastics.

In an industrial environment, rubber/silica compounds typically require three subsequent mixing/cooling steps in order to provide optimal size of the silica aggregates and their relatively uniform distribution throughout the rubber matrix. An alternative approach is considered where silica particles are directly grown in the rubber matrix by using the sol-gel reaction. In this way the obtained in-situ nanocomposites are prepared in a simpler one step method, instead of three, by growing the silica in the rubber matrix. Additionally, this represents also a more cost-effective production approach because no intensive subsequent mixing (for break-up and distribution of the aggregates) or addition of coupling agents is needed for achieving good dispersion of the silica particles.

1.3.1. In-situ rubber/silica nanocomposites via sol-gel reaction

The sol-gel reaction has been extensively used to create novel (hybrid) nanocomposites.\textsuperscript{42-46} The first to exploit the sol-gel reaction was J.E. Mark in 1981 who produced silica particles in (dimethylsiloxane) rubber.\textsuperscript{47} Three routes can be distinguished for the synthesis of these materials via the sol-gel process. The first is the solution method where the rubber is dissolved in a suitable solvent and the sol-gel reaction proceeds in the obtained rubber solution.\textsuperscript{48} The second is in-situ polymerization where the polymerization and the sol-gel reaction are performed simultaneously.\textsuperscript{49,50} The third method is the swelling method performed in two steps: in the first step the rubber is swollen in an alkoxide precursor and in the second step the swollen rubber is immersed in the catalyst solution where the
sol-gel reaction may proceed via basic or acid conditions for obtaining in-situ silica.\textsuperscript{18} Several factors such as the water/silane ratio, the type and amount of catalyst, the type of precursor, the temperature and the nature of solvent/rubber matrix have a significant effect on the sol-gel reaction and, consequently, result in silica with different physical and chemical properties.\textsuperscript{51-55}

Sol-gel reaction via the swelling method was extensively applied in different rubbers such as NR,\textsuperscript{56,57} SBR,\textsuperscript{58} epoxy resin,\textsuperscript{59} poly (dimethylsiloxane)\textsuperscript{60} and thermoplastics like polypropylene\textsuperscript{61} and poly(methylmethacrylate)\textsuperscript{62} on lab-scale only, with no attempts for industrial production of the in-situ nanocomposites. In general, there are several reasons we might consider responsible for the non-commercialization of the silica in-situ nanocomposites, such as: long reaction times (24 - 48 h) required to obtain silica, relatively low conversion of TEOS and possibly high amounts of alcohol (by-product of the sol-gel reaction) to be removed.

1.3.2. Sol-gel chemistry for silica formation

The production of amorphous silica via the sol-gel reaction was for the first time reported in 1968 by Stober et al.,\textsuperscript{63} who prepared silica particles in a aqueous solution using tetraethoxysilane (TEOS) as precursor and ammonia as catalyst. In this process, the alkoxide silane precursors undergo hydrolysis and polycondensation reactions (Figure 1.9) in the presence of acid or base catalysts to form silica particles.\textsuperscript{64,65}
The sol-gel reaction proceeds via several simultaneous chemical reactions, resulting in the formation of various intermediate compounds. Under acidic conditions the hydrolysis reaction begins with protonation of an alkoxy group which decreases the electron density around the silicon atom, allowing an easier attack by water molecules. The water molecule approaching the alkoxide will acquire a partially positive charge allowing easier detachment of the alkoxy group leading to formation of the first hydrolyzed intermediate \(^{18,19}\) (Figure 1.10). The hydrolysis rate increases with additional substitution of alkoxy groups from the precursor, due to decreased steric hindrance around the silicon atom. Under acidic conditions the condensation reaction is slower than the hydrolysis and it additionally slows down upon an increasing number of siloxane linkages to the central silicon atom in the intermediate compounds and eventually results in the formation of weakly branched silica networks.

Under basic conditions hydroxyl ions start the hydrolysis by substituting an alkoxy group at the silicon atom with a hydroxyl group (Figure 1.11). The substitution of alkoxy groups with hydroxyl groups will reduce the electron density around the
silicon atom because the hydroxyl group is a strongly electron withdrawing group and increases the reactivity of the alkoxide. Thus, the rate of hydrolysis will increase with each subsequent substitution of the alkoxy groups.\textsuperscript{18,19}

![Figure 1.11. Reaction mechanism for base-catalyzed sol-gel reaction.\textsuperscript{18}](image)

Under basic conditions the condensation reaction proceeds faster than the hydrolysis and it increases with the number of siloxane linkages on the intermediate compounds, resulting in particles with larger sizes than observed under acidic conditions. The sol-gel reaction under basic condition proceeds via an anionic mechanism during which negatively charged species are formed that tend to repel each other. Thus single particles will rather grow more individually into larger particles than form silica networks, as under acid conditions.\textsuperscript{66,67}

\section*{1.4. Mechanical properties of rubber/silica nanocomposites}

\subsection*{1.4.1. Static mechanical properties of rubber}

Some of the factors which determine the physical and mechanical behaviour of a rubber are the size and flexibility of the chemical groups in the polymer chain backbone, the susceptibility to deformation of inter-atomic bonds and the strength of inter-chain interactions.\textsuperscript{1} Values for some typical mechanical properties of non-filled, crosslinked rubber materials, such as tensile strength, hardness, modules and elongation at break, are shown in Table 1.3.
When a stress-strain test is performed on rubber samples the three most important properties tested are the Young’s modulus, the tensile strength and the elongation at break. The tensile strength corresponds to the force needed to break the rubber specimen and the elongation at break is the maximum elongation the sample can undergo before breaking. The measurement of Young’s modulus in rubber materials is very difficult, because the stress needed to deform a rubber sample is small and usually special load cells are needed for a very precise measurement. Therefore, in most cases the ‘modulus’ is measured as the stress at a particular strain and it represents the stiffness of the material. Other mechanical properties used to characterize the rubber materials are hardness, compression set and abrasion resistance.\textsuperscript{1,2,3}

Rubber materials are rarely used in their pure form because they have weak mechanical properties and therefore usually are reinforced by fillers.\textsuperscript{1,2,3} The improvement in mechanical properties by addition of fillers is commonly called reinforcement. The type and amount of filler will have a large impact on the physical properties of the rubber (Figure 1.12).

\begin{table}[h]
\centering
\caption{Physical properties of non-filled crosslinked NR, SBR and EPDM.\textsuperscript{32,68}}
\begin{tabular}{|c|c|c|c|c|}
\hline
Material & Specific density [g/m\textsuperscript{3}] & Hardness (Shore A) & Tensile strength [MPa] & Elongation at break [%] \\
\hline
NR & 0.92-1.03 & 30-100 & \textasciitilde 17.2 & 300-800 \\
SBR & 0.94 & 30-90 & \textasciitilde 20.7 & 450-500 \\
EPDM & 0.86 & 30-90 & \textasciitilde 24.1 & 100-700 \\
\hline
\end{tabular}
\end{table}
Active and non-active fillers have a different impact on the mechanical properties of the rubber material. The addition of a certain amount of active fillers (silica or carbon black) increases the hardness of the rubber compound, improves its tensile strength (to a certain amount of filler) and the abrasion resistance. However, with the addition of filler the viscosity of the rubber composite is significantly increased which can seriously limit the processing. The compression set increases with filler content significantly, which corresponds to lower elasticity. The tuning of the properties of the final rubber material in correlation to the filler type and amount are fully related to the application requirements.

### 1.4.2. Dynamic mechanical properties of rubber

For polymers dynamic mechanical properties generally refer to the responses of a material under periodically varying strains.\(^3\)\(^4\) They are strongly dependent on temperature, frequency, presence of fillers and the extent of deformation. The dynamic mechanical properties are expressed with the storage \(G'\), loss modulus \(G''\)
and the loss angle determined from their ratio \( \tan \delta = \frac{G''}{G'} \). The elastic modulus measures the elasticity of the material, i.e. its ability to store energy whereas the loss (viscous) modulus measures the lost of energy as heat, i.e. its ability to dissipate energy. The ratio of the two moduli is a measure of the dissipated energy relative to the stored energy during deformation. A schematic representation of the dynamic mechanical properties is given in Figure 1.13.

![Figure 1.13. Dynamic mechanical properties of non-filled rubber compound.](image)

The storage modulus is not strain dependant in the low strain region (< 10 % strain) showing a linear plateau, whereas for higher strains (> 10 % strain) it shows non-linear dependence slowly approaching another lower plateau. The Payne effect is designated as the difference between the low-strain modulus and the high-strain modulus. The particle (aggregate) size, dispersion, type and amount of filler are considered to influence mostly the modulus at low strain, while the rubber-filler interactions usually play a major role in the modulus at high strain.\(^{70-76}\) The Payne effect\(^{77-85}\) is usually explained by the breaking of the filler-filler network. However, new insights into this phenomenon\(^{86-88}\) show that rubber-filler interaction play also very important role via the so-called trapped entanglements. The loss angle (\( \tan \delta \)) is lower for filled than for unfilled compounds at low strains while at higher strains the opposite is valid. The strain dependence of the loss angle is usually related to the breakage and reformation of the filler network in the filled compound.\(^{77,89}\)
1.5. Aim of thesis

In summary, the silica dispersion (aggregate form) within a polymer matrix, which is an extensively time and energy consuming process, can be improved by applying the sol-gel reaction as an alternative approach. The sol-gel reaction is expected to surpass the dispersion issues enabling improvement of the mechanical properties. The rubber/silica nanocomposites prepared via a sol-gel reaction show significantly improved mechanical properties, usually ascribed to improved rubber-filler interactions. However, due to the scarce availability of information tackling the nature of the rubber-silica interactions when silica is prepared by sol-gel reaction, we conducted a more detailed study regarding the silica structure and surface. This study is expected to provide a better understanding of the type of interactions between the silica and the polymer matrix and thus the improved mechanical properties. In addition, the thesis also aims to gain fundamental understanding of the mechanism of the silica formation via sol-gel reaction in rubber materials considered directly responsible for the unique structure (and surface) of the formed silica. Moreover, a kinetic study of the sol-gel reaction at higher temperatures (up to 120 °C) is conducted in order to reveal the possibilities of continuous production of the in-situ nanocomposites via a reactive extrusion process.

1.6. Outline of thesis

In Chapter 1 of this thesis the current state of the art in the field of nanocomposites is given, with emphasis on the preparation and properties of nanocomposites produced via the sol-gel reaction. Outlined are also the objectives of the study, i.e. to provide a thorough understanding of the mechanism and the kinetics of the sol-gel reaction in a rubber matrix and to correlate the structure of the in-situ synthesized silica to the properties of the rubber nanocomposites. To that purpose, the in-situ rubber/silica nanocomposites were prepared via the sol-gel reaction, using TEOS as precursor and hexylamine as catalyst.
The effects of different reaction parameters, i.e. amount of precursor, reaction time, temperature and type of rubber, on the structure of the prepared in-situ nanocomposites (content, size, and dispersion of silica) are shown in Chapter 2. Transmission electron microscopy (TEM) was used to study the dispersion of the silica particles in the in-situ nanocomposites. The amount of bound rubber was evaluated and it was correlated to the rubber-silica interaction.

The kinetics and the mechanism of the sol-gel reaction in a rubber matrix were studied in detail by performing time-resolved solid-state NMR and SAXS experiments. The results presented in Chapter 3 indicate that the sol-gel process in a rubber matrix adopts the emulsification process behaviour, where hexylamine used as catalyst, behaves as surfactant forming inverse micelles with enclosed water in a TEOS-swollen rubber matrix. In addition, in this chapter the kinetics of silica growth is followed by time-resolved SAXS and solid state NMR.

The structural investigation of the in-situ synthesized silica particles, presented in Chapter 4, was performed using solid state NMR and MS-TGA-IR. For the first time it is shown that so-called ‘hairy’ silica particles, with hexylamine and remnant ethoxy groups residing predominantly on the silica surface, are obtained via this process. This ‘hairy’ silica surface results in a more hydrophobic nature of the silica particles and in stronger rubber-silica interactions.

In Chapter 5 the properties of the in-situ nanocomposites produced in both static and dynamic conditions (mixer) are discussed and compared to those of the conventionally prepared rubber/silica nanocomposites. The measurements with a Rubber Process Analyzer (RPA) indicated a strong reinforcement of the rubber matrix by the in-situ silica at much lower silica loadings in comparison to the conventional rubber/silica nanocomposites. This strong reinforcement of the in-situ prepared nanocomposites can be ascribed to the stronger interactions between the in-situ made silica particles and the rubber matrix, the presence of trapped entanglements and bound rubber content.

In-situ nanocomposites were successfully produced via reactive extrusion, which was one of the goals in this thesis. The in this way obtained in-situ nanocomposite had a maximum loading of 3.2 wt% silica and possessed a uniform
particle dispersion and very good properties. Chapter 6 contains the technological assessment of this study. The possibilities for industrial application of the sol-gel process to obtain rubber-silica nanocomposites with excellent properties are discussed.
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Influence of reaction parameters on structure of in-situ rubber/silica nanocomposites synthesized via sol-gel reaction

Abstract

In-situ silica was synthesized in non-vulcanized rubber such as NR (natural rubber), SBR (styrene-butadiene rubber) and EPDM (ethylene-propylene-diene ter-polymer) using the sol-gel method with tetraethylorthosilicate (TEOS) as silica precursor and hexylamine as catalyst. The effect of the reaction parameters, such as the amount of TEOS, the reaction time (15 - 120 min) and the type of rubber were explored. Transmission electron microscopy (TEM) is used to study the gradient in silica content and particle size over the sample thickness. An excellent dispersion of silica was obtained for all rubbers, even for the very apolar EPDM, without the use of any additives to improve the dispersion. The excellent dispersion and the larger surface area (small particle size) of the silica provided higher bound rubber contents of the in-situ nanocomposites as compared to the conventional nanocomposites where pre-synthesized silica was mixed with rubber.
2.1. Introduction

Driven by the demands for a stronger, tougher and lighter-weight material, a new group of nanocomposite materials was developed, composed of an inorganic filler and an organic polymer matrix where the filler size is in nanometer range (10 - 100 nm). These nanocomposites are also called hybrid nanocomposites, because they combine the advantages of both materials: rigidity, thermal stability and barrier properties from the filler and flexibility, ductility and processability from the polymer. The particulate nano-fillers have a high surface area-to-volume ratio, resulting in a significant improvement of the mechanical properties of the composite. In the rubber industry a wide variety of particulate nano-fillers are used, among which most popular are carbon black and silica. In the rubber industry silica is increasingly being used, because of the improved balance of abrasion, wet grip and rolling resistance, also known as the magic triangle of properties which is particularly useful for high-performance tires (green tires). Conventional mixing of silica and rubber is a serious challenge, when a uniform silica particle dispersion needs to be achieved. The hydroxyl groups residing on the surface result in highly polar nature of the silica. Strong hydrogen bonds are developed between the silica particles resulting in silica agglomerates with various sizes. The difficult mixing of rubber and silica usually results in large silica aggregates, non-uniformly distributed throughout the rubber matrix, yielding conventional rubber/silica nanocomposites with non-optimum mechanical properties. Industrial mixing requires several steps and is commonly accommodated by using a coupling agent (e.g. TESPT), which provides a better dispersion of the aggregates through the matrix.

An alternative way to prepare hybrid nanocomposites is offered by the sol-gel reaction, which can be performed under mild conditions via three routes: the solution method, the swelling and the in-situ polymerization. The sol-gel reaction avoids the mixing steps and the formation of silica aggregates and provides instead in-situ nanocomposites with single silica particles, uniformly distributed through the rubber matrix. The sol-gel reaction consists of two basic
reactions i.e. hydrolysis of the tetraalkoxysilane, followed by condensation reactions. These reactions occur in the presence of water and catalyst, resulting eventually in the formation of silica particles.\textsuperscript{16} From a practical point of view the swelling method is most convenient where the silica formation via the sol-gel reaction occurs directly in the rubber matrix. The sol-gel reaction consists of complex reaction sequences influenced by several parameters, such as pH, reaction temperature, reaction time, catalyst type and concentration, water content, structure and concentration of the tetraalkoxy silane and the type of rubber.\textsuperscript{17-20} Variations in these reaction parameters will result in various morphologies of the prepared rubber/silica nanocomposites and consequently, in different mechanical properties. The improved mechanical properties reported for \textit{in-situ} rubber/silica nanocomposites,\textsuperscript{21,22,23} as compared to conventional nanocomposites has been ascribed to the uniform silica particle dispersion without any pronounced aggregation and the possibility of having stronger rubber-silica interactions due to the specific structure of the formed \textit{in-situ} silica.\textsuperscript{24,25} Various studies have suggested, but not yet prove that the stronger rubber-silica interactions may be a consequence of the lower amount of silanol groups present on the \textit{in-situ} silica surface. The strength of the silica/rubber interactions can to a certain extent be estimated by the bound rubber content\textsuperscript{26-28} which is defined as the remaining rubber on the filler surface after a thorough extraction of the free rubber in an uncured rubber sample using an appropriate solvent.

So far, the sol-gel reaction has been studied extensively in aqueous solution and solution of rubber using different reaction parameters. However, limited information is available on the influence of the different reaction parameters on the sol-gel reaction when performed in the rubber matrix and on the morphology of the \textit{in-situ} nanocomposites produced. This study aims to show the influence of the reaction conditions i.e. the amount of TEOS, the reaction time and the type of rubber on the nanocomposite structure and on the bound rubber content for \textit{in-situ} nanocomposites prepared via the swelling method.
2.2. Experimental section

2.2.1. Materials

The silica precursor, TEOS and the (n-hexylamine) catalyst were purchased from Aldrich and used as received. The characteristics of the three rubbers, namely natural rubber (NR; Tun Abdul Razak Research Centre), styrene-butadiene rubber (SBR; Lanxess) and ethylene-propylene-diene rubber (EPDM; Lanxess), are shown in Table 2.1. The type of silica used for conventional mixing is Zeosil 1165 MP produced by Rhodia, known as a highly dispersible (HD) silica commonly used in the rubber industry for the production of ‘green’ tires. It has a BET surface area of 150 m²/g and an average particle size of 10 - 20 nm.

<table>
<thead>
<tr>
<th>Rubber type</th>
<th>NR SMR L</th>
<th>EPDM Keltan 512</th>
<th>SBR VSL 5025-0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition [wt%]</td>
<td>Isoprene (1,4-cis)</td>
<td>Ethylene/Propylene/ENB</td>
<td>1,2-vinyl/1,4-styrene</td>
</tr>
<tr>
<td>Impurity [wt%]</td>
<td>0.5</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>$M_w$ [kg/mol]</td>
<td>~ 800</td>
<td>260</td>
<td>450</td>
</tr>
<tr>
<td>Mooney viscosity (ML (1+4))</td>
<td>50-60 (100°C)</td>
<td>46 (125°C)</td>
<td>69 (100°C)</td>
</tr>
<tr>
<td>$T_g$ [°C]</td>
<td>-65</td>
<td>-54</td>
<td>-20</td>
</tr>
</tbody>
</table>

It was difficult to determine the exact molecular weight of the NR using gel permeation chromatography (GPC), because there was always residual gel. Literature suggests an approximate $M_w$ value of $8 \times 10^5$ g/mol and $M_w/M_n = 2.3$.

Preparation of conventional NR nanocomposite

The conventional nanocomposites were prepared in an internal mixer ($V = 390$ cm³) with tangential rotors and a fill factor of ~ 70 vol%. The starting temperature was 50 °C and the rotor speed was adjusted to reach temperatures above 140 °C. Usually for 10 to 15 wt% silica, a rotor speed of 110 rpm was enough to achieve the desired temperature (140 - 170 °C). However, for mixture with 1 wt% silica the rotor speed was increased up to 130 rpm, because this small
amount of silica does not significantly contribute to a torque increase. The actual temperature of mixing was kept at 140 - 160 °C for all compounds, regardless whether a coupling agent was used or not, in order to maintain equal processing conditions for all samples. In the presence of TESPT coupling agent the temperature must be above 140 °C to start the silanization reaction but below 170 °C to prevent crosslinking of the rubber due to sulphur release from the coupling agent.

The mixing was performed in two steps. In the first step ZnO, stearic acid, half the amount of silica and half the amount of TESPT (if used) were added to the rubber and in the second step the remaining components were added. The mixing time of all components in the internal mixer was approximately 6 min. At the end, the so-called ‘dump’ temperature of the mixture was measured. The dump temperature should be always above or equal to 140 °C to ensure that the silanization reaction is completed. The compound formulations used are shown in Table 2.2.

*Table 2.2 Mixing parameters for conventional NR nanocomposites with ~1 and 15 wt% silica.*

<table>
<thead>
<tr>
<th>Components [phr]</th>
<th>Silica content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 phr (0.95 wt%)*</td>
</tr>
<tr>
<td>NR/SMR L (0.5 % non rubber content)</td>
<td>100</td>
</tr>
<tr>
<td>Silica/ZEOSIL 1165 MP</td>
<td>2</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
</tr>
<tr>
<td>Oil/Sunpair 2280</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>Silane/TESPT</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>114</td>
</tr>
</tbody>
</table>

*Coupling agent (TESPT)

* Silica content of conventional nanocomposites as determined by TGA

It should be noted, that the silica content as measured by TGA was lower than when calculated from Table 2.2. In the rubber industry, phr (parts per hundred rubber) is the commonly used unit for quantity, because it simplifies the
formulations for the preparation of the conventional rubber/silica nanocomposites. Further in the text reference is always made to wt% silica instead of phr. It is noted that the content of inorganics (silica and ZnO) in the conventional nanocomposites was determined by TGA (averaged over two measurements) and the silica content was obtained after subtraction of the known ZnO content. The amount of TESPT was 8 wt% with respect to the amount of silica added to the rubber. Even though the rubber compounds were not intended for vulcanization, stearic acid and ZnO were additionally added in order to approximate the preparation conditions of industrial rubber/silica mixtures. ZnO is used as an activator and stearic acid as a plasticizer and a co-activator for sulphur vulcanization (when performed).

**Preparation of in-situ rubber/silica nanocomposite by swelling sol-gel method**

The in-situ rubber/silica nanocomposites were prepared as described by Ikeda et al.\(^ {18} \) for NR, SBR and EPDM. Compression moulded rubber sheets with dimensions of 10 x 10 x 1.5 mm\(^3 \) were swollen in TEOS at 40 °C until a certain swelling degree was reached and then immersed in a catalyst solution at 40 °C for a particular reaction time. The obtained in-situ nanocomposites were finally dried for 72 h at 50 °C under vacuum. A catalyst concentration in water of 0.096 mol/l and a weight ratio H\(_2\)O:TEOS (5:1) were chosen to provide a maximum amount of silica, as suggested by Ikeda et al.\(^ {18} \) For the three types of rubber the amount of TEOS was varied by varying the swelling time. In addition, the reaction time was also varied between 15 - 120 min for a constant amount of TEOS.

The TEOS content (in wt%) after swelling was determined according to the following equation:

\[
Wt\% \text{ TEOS} = \frac{w_{\text{TEOS}}}{w_{\text{rubber}} + w_{\text{TEOS}}} \cdot 100
\]  

where \( w_{\text{TEOS}} \) is the mass of TEOS swollen in the rubber matrix in (g) and \( w_{\text{rubber}} \) is the weight of the rubber sample before swelling in (g).

The theoretical silica yield was calculated assuming that 1 mol of TEOS corresponds to 1 mol of silica (SiO\(_2\)) as shown in the following equation:
Si(OC₂H₅)₄ + 2 H₂O $\Rightarrow$ SiO₂ + 4 C₂H₅OH \hfill (2.2)

\[ w_{\text{silica}}^{\text{theoretical}} = \frac{M_{\text{silica}} \cdot W_{\text{TEOS}}}{M_{\text{TEOS}}} \text{ [g]} \]

\[ Wt\%_{\text{silica}}^{\text{theoretical}} = \frac{w_{\text{silica}}^{\text{theoretical}}}{w_{\text{rubber}} + w_{\text{silica}}^{\text{theoretical}}} \cdot 100 \hfill (2.3) \]

where, \( M_{\text{silica}} \) is the molar mass of SiO₂, 60.08 g/mol and \( M_{\text{TEOS}} \) is the molar mass of TEOS, 208.33 g/mol. The conversion of TEOS (in \%) is defined as following:

\[ \text{TEOS conversion} = \frac{Wt\%_{\text{silica}}^{\text{experimental}}}{Wt\%_{\text{silica}}^{\text{theoretical}}} \cdot 100 \% \hfill (2.4) \]

where, \( Wt\%_{\text{silica}}^{\text{experimental}} \) is the silica content as determined by TGA.

**Bound rubber determination**

*In-situ* and conventional rubber/silica nanocomposites with various silica amounts were immersed in THF, which is good solvent for the three rubbers. The ratio between the rubber/silica nanocomposites and the solvent was kept constant (2 \% w/v) and the samples were immersed in the solvent for 48 h at room temperature while shaking. The residues were dried for 72 h at 50 °C under vacuum. The bound rubber content was calculated as following:

\[ \text{Wt\% Bound rubber content} = \frac{W_{\text{residue}} - W_{\text{silica}}}{W_{\text{original}} - W_{\text{silica}}} \cdot 100 \hfill (2.5) \]

where, \( W_{\text{residue}} \) is the weight of the sample after solvent treatment in (g), \( W_{\text{original}} \) is the weight of sample before solvent treatment in (g) and the \( W_{\text{silica}} \) is the weight of silica in (g) in the nanocomposite.
2.2.2. Characterization

**Thermo-gravimetric analysis (TGA)**

A Q500 TGA from TA Instruments was used for the quantitative determination of the silica content in the rubber/silica nanocomposites. Samples were heated in an air atmosphere with 10 °C/min up to 900 °C to provide complete oxidation of the hydrocarbon rubber. The residue after this thermal treatment is assumed to be composed of silica only. All measurements were repeated at least twice and an average of the results was used.

**Transmission Electron Microscopy (TEM)**

Morphological studies were performed using a Tecnai 20 transmission electron microscopy (TEM), operated at 200 kV. It should be noted, that later in the text it will be referred to structure and not morphology of the nanocomposites. Ultrathin sections (~ 70 nm) were prepared using a Leica Ultracut S/FCS microtome at -110 °C using DMSO. Chemical staining was not required, since the electron density of silica is much higher than that of the rubber matrix. For easier handling while cryo-cutting, some of the samples were treated with gamma irradiation (100 kGy) at Gammaster International BV, Ede. This provided extra stiffness to the material as a result of crosslink formation. Details on sectioning will be explained extensively later in this chapter.

2.3. Results and Discussion

2.3.1. Effect of TEOS amount on in-situ NR nanocomposites

The amount of TEOS is one of the reaction parameters of the sol-gel reaction studied extensively for alcoholic\textsuperscript{30-32} and rubber solutions.\textsuperscript{33,34} A significantly larger particle size was shown for higher TEOS contents. However, a correlation between the particle size and the TEOS amount has not been found so far for the swelling method. For that purpose, in-situ NR/silica nanocomposites have been prepared with various amounts of TEOS (and constant reaction time of 2 h) as
depicted in Table 2.3.

Table 2.3. Preparation of in-situ NR nanocomposites for 2 h reaction time at 40 °C for various amounts of TEOS.

<table>
<thead>
<tr>
<th>Swelling time [h]</th>
<th>wt % TEOS</th>
<th>wt% theoretical silica</th>
<th>wt% experimental silica</th>
<th>Conversion TEOS [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>22.5</td>
<td>6.5</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>30</td>
<td>14</td>
<td>46</td>
</tr>
<tr>
<td>5</td>
<td>67</td>
<td>37</td>
<td>20</td>
<td>57</td>
</tr>
<tr>
<td>10</td>
<td>74</td>
<td>45</td>
<td>28</td>
<td>63</td>
</tr>
<tr>
<td>24</td>
<td>77</td>
<td>49</td>
<td>40</td>
<td>82</td>
</tr>
</tbody>
</table>

The conversion of TEOS during the sol-gel reaction will be always less than 100 % because the theoretical silica is always higher than the experimentally determined silica content. The TEM images of the in-situ NR nanocomposites with 6 - 28 wt% silica are shown in Figure 2.1. The sample with 40 wt% silica is not considered, because it was too brittle to handle. This amount of silica corresponds well with the silica content obtained by Ikeda et al.\textsuperscript{18} for significantly shorter reaction time. The in-situ NR nanocomposites show a relatively uniform silica dispersion with the occasional appearance of particle aggregates (marked with red circles).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.jpg}
\caption{Effect of TEOS content on morphology of NR/silica nanocomposites for 2 h reaction at 40 °C time: (a) 50 wt%, (b) 60 wt%, (c) 67 wt% and (d) 74 wt% TEOS. Presence of silica aggregates indicated with the circles.}
\end{figure}

Figure 2.1 and the results in Table 2.3 show that by increasing the TEOS content from 50 to 74 wt% an increase in silica content from 6.5 to 28 wt% is obtained, accompanied with an increase in the average particle size from 27 to 40 nm and
higher conversion of TEOS (see Table 2.3). The increase of the particle size with the TEOS content is explained as follows: in order to preserve the ratio of TEOS:H₂O (1:5), the higher TEOS concentration in the rubber consequently requires a higher amount of aqueous catalyst solution. As a side effect the amount of the hydroxyl ions is increased and as a consequence the hydrolysis and the condensation reactions are enhanced. In addition, the higher amount of TEOS (and hydroxyl ions) will provide a higher concentration of available hydrolyzed and non-hydrolyzed TEOS in the vicinity of the growing particles. This is particularly important when the sol-gel reaction is performed in a rubber, where serious limitations in the mobility of the reactants (TEOS and catalyst solution) are imposed by the rubber network of chains.

It must be noted that by rubber network we are referring only to a physical network of chains because the NR is not crosslinked and therefore no chemical bonds exist between the rubber chains. The availability of more molecules allows the silica particles to grow to a larger particle size for same reaction time. However, despite the evident effect on the particle size, it is not clear whether the higher availability of hydrolyzed TEOS molecules will also promote the formation of new silica particles. For that purpose, the particle number density was determined of the in-situ NR nanocomposites by manually counting the particles from the TEM images in a volume of 0.1 μm³ and section thickness of 70 nm (set value on the cutting instrument). The number of particles (averaged over 3 images) indicates no significant change with increasing TEOS content, as shown in Figure 2.2.
Figure 2.2 suggests that by the increase in TEOS content the particle size is predominantly affected and not the particle number density. It should be noted that for the sample with 74 wt% TEOS (28 wt% silica) a somewhat lower particle number was obtained. This can be ascribed to the error introduced while counting the particles, due to enhanced presence of silica aggregates. The individual particles in the aggregate cannot be easily distinguished and precisely counted. These aggregates are more predominant for the samples with higher silica contents (> 14 wt%) and are not taken into account during counting.

2.3.2. Effect of reaction time on in-situ NR nanocomposite structure

The reaction time studied extensively only in solutions.\textsuperscript{30,31,34} is another parameter which has an effect on the size of the silica particles and the structure of the in-situ nanocomposites obtained via sol-gel reaction. In order to study this parameter for our particular system, where the rubber is swollen in the silica precursor in-situ nanocomposites were prepared with a constant TEOS content of 50 wt% and a constant amount of catalyst solution (TEOS:H\textsubscript{2}O = 1:5) varying only the reaction time from 15 - 120 min at 40 °C, as shown in Table 2.4.
Table 2.4. Silica content obtained for in-situ NR nanocomposites prepared at different reaction times at 40 °C with 50 wt% TEOS.

<table>
<thead>
<tr>
<th>Reaction time [min]</th>
<th>wt% silica</th>
<th>Particle size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.8</td>
<td>16 ± 3</td>
</tr>
<tr>
<td>30</td>
<td>2.3</td>
<td>20 ± 3</td>
</tr>
<tr>
<td>60</td>
<td>3</td>
<td>23 ± 3</td>
</tr>
<tr>
<td>120</td>
<td>6.5</td>
<td>27 ± 3</td>
</tr>
</tbody>
</table>

Table 2.4 shows a clear increase in the silica content with the reaction time. Usually, the sol-gel reaction is performed at very long reaction times in order to achieve the highest possible silica content. However, our primary interest was not to achieve the highest silica content, but to study the structural changes (silica content, particle size, shape and silica dispersion) in the obtained in-situ nanocomposites, as a function of reaction time as shown with the TEM images in Figure 2.3.

![Figure 2.3. Effect of reaction time at 40 °C with 50 wt% TEOS on the morphology of in-situ NR nanocomposites: (a) 15 min, (b) 30 min, (c) 60 min and (d) 120 min.](image)

The TEM images in Figure 2.3 show an increase of the average particle size from 16 to 27 nm with an increase of reaction time. It is noted that at low silica contents (1.8 wt%) the spherical shape of the particles is not fully developed. However, at longer reaction time the particles tend to develop a fully spherical shape and become more monodisperssed. This effect was also observed in previous studies when silica particles were formed in solution. It seems typical for the early stages of silica formation, that the particle shape is still somewhat fuzzy. This is ascribed to the addition of the relatively larger silica species in the early stages of the silica
growth.\textsuperscript{35,36} The increase of the particle size and the particle number density with the reaction time is shown in Figure 2.4.

Figure 2.4. (a) Average particle size as function of reaction time and (b) particle number (per \( V = 0.1 \ \mu m^3 \)) vs. average particle size as function of reaction time (15, 30, 60 and 120 min) at 40 °C with 50 wt% TEOS.

Figure 2.4 (a) shows initially very fast increase of the particle size that later continues to increase with a slower growth rate. Similar observations were reported in earlier studies\textsuperscript{37,35} of the silica growth only in solution, where the particle size after longer reaction times approached a plateau. The reason for the decrease in growth rate (sol-gel under basic conditions) might be due to the reduction of available silica reactive intermediates, hence less negative charges on the growing silica particles. The amount of charge depends on the degree of condensation which is highest at the beginning of the silica formation resulting in fast particle growth and lower towards the end resulting in slower growth. The time required for the particle size to reach a plateau (in rubber or solution) varies for each system, because it strongly depends on the reaction parameters (water and catalyst concentration, temperature, type of solvent or rubber matrix). The fast silica growth in the initial stages of the reaction (16 nm in 15 min) may be useful for the industrial application of the sol-gel reaction in rubber. Figure 2.4 (b) shows that the particle number density does not change significantly within the first 60 min reaction time, while a clear increase is observed for a reaction time of 120 min. A
longer reaction time allows more catalyst solution to diffuse into the rubber matrix and, thus, to contribute not only to the particle growth, but also to the formation of new particles. Interestingly, in the *in-situ* NR nanocomposites the silica particles are formed preferentially at the edges of large spherical domains (0.2 nm - 1.5 \( \mu \)m) as shown in Figure 2.5. This phenomenon has been observed earlier in NR conventional nanocomposites prepared with HD silica\textsuperscript{38,39} and was assigned to the original NR-latex particles present in the NR matrix.

![Figure 2.5. Spherical domains in in-situ NR nanocomposite with 1.8 wt% silica, reaction time of 15 min at 40 ºC with 50 wt% TEOS.](image)

The rubber particles in the original NR latex are stabilized with proteins, which reside on the surface and prevent them from coagulating. The proteins are usually difficult to remove and some of them remain in the rubber after its coagulation into the solid material. The residual proteins on the edges of the rubber particles locally increase the polarity of the NR matrix, attracting more catalyst solution that promotes silica formation on the edges of these domains.

**2.3.3. Silica gradient in in-situ NR nanocomposites**

The sol-gel reaction, used to prepare the *in-situ* nanocomposites under static conditions, is a diffusion dependent process, where TEOS and the catalyst solution diffuse in the rubber matrix and initiate hydrolysis and condensation reactions resulting in silica formation. In principle, the diffusion of the catalyst solution occurs from all sides of the sample, but here only the diffusion occurring from the
top and bottom of the sample will be considered, since this is truly limiting for the 1.5 mm thick samples. The sol-gel reaction first starts on the sample surface and progresses further along the sample thickness. Therefore, it is expected that in the centre of the rubber sample silica formation begins with a certain delay determined by the diffusion path of the catalyst solution. The actual silica gradient was studied in an in-situ NR nanocomposite prepared with 50 wt% of TEOS for a reaction time of 2 h at 40 °C. For this purpose the sample was cryo-cutted as displayed in Figure 2.6.

![Figure 2.6. Schematic drawing of cutting procedure of rubber sample for determination of silica gradient (---) cube cutted from middle of in-situ NR nanocomposite.](image)

The silica gradient was studied with both techniques, TGA and TEM, in each particular layer as shown schematically in Figure 2.6. The silica content was determined for each layer separately as designated with the TGA area. Three layers from the specimen were prepared for TEM observation: a surface layer, an intermediate and a centre layer. The results in Figure 2.7 confirm a gradient in silica content and particle size, varying from 7.4 wt% and 35 nm at the surface to 4.4 wt% and 16 nm in the centre of the sample, respectively.
Two reasons for the observed variation in particle size and silica content along the sample thickness can be suggested: the possible non-uniform concentration profile of the TEOS along the sample thickness and the physically and chemically retarded diffusion of the catalyst solution. The rubber sample after swelling in TEOS is immediately immersed into the catalyst solution. It is expected that the amount of TEOS is the highest on the surface where the sample is directly exposed to TEOS and to gradually decrease towards the centre.

Additionally, the sol-gel reaction in the surface layer of the sample will start almost immediately when the catalyst solution enters the sample, while in the centre layer the effective reaction time will be shorter. In the centre layer the reaction starts with a certain delay, i.e. only when the catalyst reaches the centre of the sample. The diffusion of the catalyst towards the centre of the sample is additionally retarded by the sol-gel chemistry occurring along the way. Considering the effect of TEOS amount and reaction times, elaborated earlier in the text, one could expect particles with larger size in the surface layer due to higher availability of the TEOS and the catalyst solution. In addition, Figure 2.7 shows that the silica particles in the centre and the intermediate layer are relatively monodispersed in size, whereas a somewhat broader size distribution is observed for the surface layer. The particle number is shown in Table 2.5.
Table 2.5. Particle number (per $V = 0.1\mu m^3$) for each layer in in-situ NR nanocomposite (2 h reaction time at 40 °C with 50 wt% TEOS).

<table>
<thead>
<tr>
<th>Layer</th>
<th>Particle size</th>
<th>Standard deviation</th>
<th>Particle number</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>centre</td>
<td>16</td>
<td>± 2</td>
<td>490</td>
<td>± 45</td>
</tr>
<tr>
<td>intermediate</td>
<td>25</td>
<td>± 3</td>
<td>480</td>
<td>± 50</td>
</tr>
<tr>
<td>surface</td>
<td>35</td>
<td>± 5</td>
<td>460</td>
<td>± 65</td>
</tr>
</tbody>
</table>

Table 2.5 shows no significant difference in the particle number density for each layer of the in-situ NR nanocomposite. The reasons for the similar particle number density could be found in the very nature of the NR. The amount of proteins and water in NR are in the range of 1 - 3 wt% and 0.1 - 0.8 wt%, respectively. In addition, in order to prevent hardening of NR during storage hydroxylamine hydrochloride ($NH_2OH-HCl$) is added. The polar amino groups present in the proteins and in the $NH_2OH-HCl$ molecules may attract more strongly the diffusing catalyst solution and, in addition, can themselves serve as potential nucleation points for the silica formation. This can result in a large number of relatively monodispersed particles uniformly distributed in the NR matrix. The gradient in silica particle size observed in the in-situ nanocomposites has not been pointed out so far and its importance is immense when reliability and consistency of the TEM and TGA results are concerned. Therefore, in this study the cryo-cutting of all samples for TEM and TGA measurements was performed approximately in the intermediate layer. The gradient in silica particle size is also expected to influence the mechanical properties which will be discussed more extensively in the chapter 5.

2.3.4. Effect of rubber matrix (NR, EPDM and SBR) on in-situ nanocomposite structure

So far the effect of the reaction parameters on the structure of the in-situ nanocomposites was only considered for NR. However, since the type of the rubber matrix may also influence silica formation and the final structure of the
nanocomposite, two additional rubbers, (ethylene-propylene diene monomer) EPDM and (styrene-butadiene rubber) SBR were studied. Unlike the NR, these materials are synthetic rubbers. NR, EPDM and SBR were used to prepare the corresponding *in-situ* nanocomposites at identical reaction conditions, i.e. TEOS amount of 33 wt% and a reaction time of 15 min at temperature of 80 °C. The chosen temperature is higher than previously used (40 °C for NR) because EPDM is not able to reach 33 wt% TEOS at 40 °C. The TEM images in the Figure 2.8 represent the resulting morphologies obtained for each rubber type.

![Figure 2.8](image)

*Figure 2.8. Morphology of NR, EPDM and SBR in-situ nanocomposites, SBR morphology and particle size distribution.*

Figure 2.8 shows the variation in the silica content for each rubber type, with the highest amount obtained for the SBR (5.5 wt%, TEOS conversion: 43.6 %), the lowest for the EPDM (1.5 wt%, TEOS conversion: 12 %) and for the NR nanocomposite somewhat in-between (3 wt%, TEOS conversion: 24 %) The TEM images show the different morphologies of the three NR, EPDM and SBR *in-situ* nanocomposites with differences in particle size, silica content (as measured with TGA) and particle number. The *in-situ* NR nanocomposite consists of monodisperse silica particles with a small average size of 18 nm. The EPDM nanocomposite contain somewhat larger silica particles while the SBR
nanocomposite shows enhanced polydispersity with particle sizes ranging between 85 and 112 nm. The particle number density obtained by manual counting of the particles from the TEM images resulted in different values for each of the three in-situ nanocomposites, as shown in Figure 2.9.

![Figure 2.9. Particle number (per V = 0.1 \(\mu\text{m}^3\)) as obtained from TEM images of the NR, EPDM and SBR in-situ nanocomposites.](image)

In summary, the in-situ NR nanocomposites show the smallest silica particles but the largest number density silica particles, while the opposite is observed for SBR. EPDM is in-between though more similar to NR. The difference in the final morphologies of the three nanocomposites can possibly be explained by the polarity (chemical structure) of the rubber and the presence of impurities that may promote or suppress silica formation via the sol-gel reaction. The polarity of rubbers is assessed via the Hildebrand solubility parameter, shown in Table 2.6.
The solubility parameter can be used to assess the compatibility between two different components. i.e. more similar values indicate better compatibility. The more polar the component is, the higher will be the solubility parameter, reaching a very high value of 48 MPa\(^{1/2}\) for the very polar water. The same TEOS amount (33 wt%) in the three rubbers is obtained for different swelling times, 16 h, 25 min and 15 min for EPDM, NR and SBR, respectively. Despite the similar solubility parameters of the three rubber types and TEOS, each rubber showed a distinctive swelling behaviour. EPDM and SBR represent the two extremes, where EPDM requires a long swelling time while SBR begins to significantly dissolve after absorbing only 50 wt% of TEOS. After swelling in TEOS the three rubbers obtained a whitish colour, which indicated that TEOS is possibly dispersed in the form of droplets that are large enough to scatter the visible light and change the colour of the sample. The size of these droplets may vary depending on the rubber type.

Regarding SBR, we don’t understand the reasons behind the particular morphology (small number density of large particles), but one possible explanation could be that TEOS droplets might be larger and more non-uniformly distributed throughout the rubber matrix. The contact between these droplets and the catalyst solution can result in silica formation and growth which is more localized in that particular area until all TEOS is exhausted, resulting eventually in larger silica particles.

In addition, SBR also has higher polarity (closer to the polar NBR rubber type in Table 2.6) when compared to NR and EPDM, which possibly promotes faster
diffusion of the catalyst solution resulting in a higher silica content (5.5 wt%). Due to the absence of polar impurities (e.g. proteins) in EPDM and SBR, the ‘nucleation effect’ as observed in NR is expected to be suppressed, giving larger emphasis on the particle growth and resulting in the formation of less silica particles with larger sizes. It should be noted that an excellent dispersion of \textit{in-situ} silica particles in EPDM was obtained, which is very difficult due to the very low polarity of this rubber. Earlier studies\textsuperscript{43} required the use of a coupling agent during the sol-gel reaction to achieve good silica dispersion, while here it was accomplished without the use of any additional chemicals (see Figure 2.8, EPDM with 0.5 μm magnification).

The reason for the good dispersion of silica particles in all \textit{in-situ} prepared nanocomposites originates most probably from the mechanism of the sol-gel reaction. Ikeda et al.\textsuperscript{18} proposed the possibility that the hexylamine catalyst can also behave as a surfactant, resulting in inverse water micelles in the TEOS-swollen rubber matrix. The hydrophobic alkyl chains of the hexylamine that reside on the interface of the inverse micelle are expected to provide steric stabilization for the growing silica particles and prevent them from aggregating.

\textbf{2.3.5. Bound rubber in NR, EPDM and SBR in-situ nanocomposites}

\textbf{2.3.5.1. Introduction of bound rubber}

Bound rubber is formed by the physical adsorption of rubber chain segments on the filler surface,\textsuperscript{44,45} forming a glassy-like immobilized layer around the particle, as schematically shown in Figure 2.10.
Bound rubber is the rubber that remains on the filler surface after solvent extraction with the non-bound rubber being dissolved. Earlier studies\(^\text{46}\) showed that the bound rubber layer actually consists of two types of layers, namely a tightly and a loosely bound layer. The tightly bound layer is in direct contact with the filler surface and consists of strongly adhering chain segments on the particle surface, while the chains of the loosely bound layer are either connected directly to the surface of the particle or tightly entangled with the chains extending from the tightly bound layer. The existence of these layers was additionally confirmed by \(^1\text{H}\) NMR relaxation measurements\(^\text{47,48}\) where three separate regions with different chain mobility were distinguished. The region with the lowest mobility originates from the tightly bound layer closest to the silica surface, the second region from the loosely bound layer with somewhat higher mobility and the third region is the bulk rubber network with the highest mobility, where the rubber chains are not restricted and may freely move. These layers were detected in both, silica and carbon black nanocomposites. The rubber-silica interactions play an important role in the bound rubber content. Stronger interactions are expected to enhance chain segment adsorption on the silica surface and result in higher bound rubber content. The strength of the rubber-silica interactions is strongly dependent on the polarity of the rubber and the silica characteristics, such as the particle size and surface chemistry.\(^\text{28,27}\)
2.3.5.2. Bound rubber in in-situ NR nanocomposites

Usually, the bound rubber content increases with silica content. However, for the in-situ NR nanocomposites a decrease in the bound rubber content was observed with increase in silica content, as shown in Figure 2.11.

![Figure 2.11. Bound rubber content (T_{room}, THF) vs. silica content for in-situ NR nanocomposite with silica particle size as running parameter. In-situ NR nanocomposites were prepared for different amounts of TEOS (50, 60, 67 and 74 wt%) and reaction time of 15 min (first point) and 2 h at 40 ºC.](image)

The decrease in the bound rubber content with increasing silica amount can be ascribed to the increase in the particle diameter from 16 to 40 nm, leading to a decrease of available surface area of the particles for interaction with the rubber. The very high bound rubber content at very low silica content (1.8 wt%) may be explained by the presence of very small silica particles (see Figure 2.1) providing a very large surface area and enough inter-particle distance (~ 50 - 200 nm) to allow full formation of the bound layer around the particle with reduced interruptions or overlap from the neighbouring particles. However, as the silica content increases, particle size also increases resulting in a decrease of the inter-particle distance (10 - 100 nm) (see Figure 2.1) and a possible overlap of the bound layers resulting in a lower bound rubber content. It should be noted, that both, the silica content and the particle size will have an effect on the bound rubber content in nanocomposites. While in the conventional nanocomposites these two parameters are easily
controlled by selecting the pre-synthesized type of silica, for the in-situ nanocomposites the situation becomes rather complicated because the silica content and the particle size cannot be separately controlled.

2.3.5.3. Effect of rubber type on bound rubber content

A series of in-situ nanocomposites were prepared for each rubber type under same reaction conditions. Different silica content and bound rubber contents were obtained, as shown in Table 2.7.

Table 2.7. Bound rubber content for NR, EPDM and SBR in-situ nanocomposites (various reaction times at 40 °C with 50 wt% TEOS).

<table>
<thead>
<tr>
<th>Reaction time [min]</th>
<th>NR [50 wt% TEOS] Silica [wt%]</th>
<th>Bound rubber [wt%]</th>
<th>EPDM [33 wt% TEOS] Silica [wt%]</th>
<th>Bound rubber [wt%]</th>
<th>SBR [50 wt% TEOS] Silica [wt%]</th>
<th>Bound rubber [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.8</td>
<td>77</td>
<td>0.8</td>
<td>0</td>
<td>2.8</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>2.3</td>
<td>76</td>
<td>1.0</td>
<td>0</td>
<td>6.3</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>3.0</td>
<td>74</td>
<td>1.7</td>
<td>2.0</td>
<td>8.0</td>
<td>0</td>
</tr>
<tr>
<td>120</td>
<td>6.5</td>
<td>71</td>
<td>2.3</td>
<td>6.0</td>
<td>10.0</td>
<td>0</td>
</tr>
</tbody>
</table>

The NR and SBR nanocomposites were prepared (swelling and sol-gel reaction) at 40 °C, while the EPDM nanocomposite was swollen at 80 °C in TEOS in order to obtain somewhat comparable amount of TEOS (33 wt% being the maximum at 80 °C) while the reaction was performed at 40 °C.

The NR nanocomposite exhibits a high bound rubber content at relatively low silica content which decreases with increase in silica content. The SBR nanocomposite dissolved completely regardless of the silica content showing no bound rubber at all. The EPDM behaviour is somewhere in-between, showing no bound rubber for low silica content (< 1.7 wt% silica) and an increase in bound rubber content with further increase of silica content. There might be several assumptions explaining the behaviour of SBR in THF. One of the reasons can be found in the similar solubility parameters $\delta$ of these two components, namely 17.8 MPa$^{1/2}$ for SBR and
19 MPa$^{1/2}$ for THF, leading to a more intensive dissolution of SBR as compared to NR and EPDM. The absence of bound rubber for the SBR nanocomposite can be ascribed to the larger particle size and the much smaller number of particles (see Figure 2.8). This may results in smaller surface area, leading possibly to the formation of a thinner bound layer around the particles.

2.3.5.4. **Bound rubber content of in-situ vs. conventional nanocomposites**

The structure of *in-situ* and conventional nanocomposites was compared at approximately the same silica contents (1 and 15 wt% silica), as shown in Figure 2.12. The conventional and in-situ nanocomposites are prepared as described in Table 2.2 and Table 2.3, respectively.

![Figure 2.12. Structure of conventional nanocomposite with coupling agent (a) and (b) compared with in-situ NR nanocomposites (c) and (d) at approximately same silica contents of 1 wt% and 15 wt%.

---

52
Figure 2.12 shows a significant difference in the morphology between these two types of nanocomposites. Uniformly dispersed single particles are observed in the \textit{in-situ} nanocomposites, whereas silica aggregates in the conventional nanocomposites. This difference resulted consequently in different bound rubber contents, as shown in Table 2.8. When compared at the same silica content the amount of bound rubber determined for the \textit{in-situ} nanocomposites was larger than that of the conventional nanocomposites, even when a coupling agent was used. The difference was more pronounced at lower silica content where the \textit{in-situ} NR nanocomposites showed a very high bound rubber content. This difference can be ascribed to the single-particle morphology of the \textit{in-situ} nanocomposites, providing a much larger surface area available for contact with the rubber matrix and to possibly stronger rubber-silica interactions caused by the different surface chemistry of the \textit{in-situ} silica particles. It should be noted that the bound rubber content in the conventional nanocomposites is not only a result of the immobilized layer around the silica aggregates, but also due to the so-called occluded rubber which represents the rubber trapped between and within the aggregates.\textsuperscript{46}

\textit{Table 2.8. Bound rubber contents (wt\%) for \textit{in-situ} and conventional NR nanocomposites.}

<table>
<thead>
<tr>
<th>Silica [wt%] (in-situ)</th>
<th>In-situ</th>
<th>Silica [wt%] (conventional)</th>
<th>Conventional</th>
<th>Conventional +CA*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>77</td>
<td>1</td>
<td>24</td>
<td>31</td>
</tr>
<tr>
<td>14</td>
<td>66</td>
<td>15</td>
<td>57</td>
<td>61</td>
</tr>
</tbody>
</table>

* Coupling agent (TESPT)

It has been suggested that \textit{in-situ} silica formed via the sol-gel reaction in a rubber matrix may contain less silanol groups on the surface than the HD silica, thus resulting in a lower polarity of the \textit{in-situ} silica.\textsuperscript{49,25} This will result in a better compatibility with the rubber and, consequently, in a higher bound rubber content leading to improved mechanical properties of the \textit{in-situ} nanocomposites. A detailed study of the surface structure of the silica particles prepared via sol-gel reaction is presented in Chapter 4.
2.4. Conclusions

It has been shown that the reaction parameters such as the amount of TEOS, the reaction time and the rubber type have great impact on the morphology (particle size and silica content) of the obtained in-situ nanocomposites. An important observation is the existence of a gradient along the sample thickness in in-situ NR nanocomposites, where particle size and silica content depend on the diffusion of TEOS and catalyst solution available along the sample thickness. Good silica dispersion was obtained in EPDM, which is highly apolar rubber for which it is difficult to achieve good silica dispersion. In contrast to the usual increase in bound rubber content with silica content, the in-situ NR nanocomposites showed the highest amount of bound rubber (BR = 77 wt%) for the lowest silica content of 1.8 wt% and then continued to decrease with increasing silica content. Finally, the bound rubber content of the in-situ nanocomposites was larger than that of the conventional nanocomposites (with a coupling agent) at equal silica loadings. This is probably due to the unique single-particle morphology of the in-situ synthesized silica.
2.5. References

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Growth mechanism of in-situ silica and kinetics of sol-gel reaction in a rubber matrix as followed by real-time SAXS and solid-state NMR

Abstract

Silica formation in a rubber matrix possibly proceeds via inverse emulsion process where the hexylamine being a catalyst, also behaves as a surfactant. The kinetics of the sol-gel reaction in the rubber matrix, as followed by the MAS-NMR method, was studied as a function of the reaction temperature (40 - 120 °C). The development of the particle size during the silica formation in the rubber matrix, as followed by the real-time SAXS revealed an initial fast increase in particle size (15 min) that decreased gradually for longer reaction times, eventually reaching a plateau. Moreover, single pulse MAS-NMR measurements showed no significant change in the structure of the silica particles after 15 and 60 min reaction time at 100 °C indicating good silica quality for short reaction time.
3.1. Introduction

In 1968 Stöber et al.,\textsuperscript{1} introduced a method for the preparation of monodispersed spherical silica particles from aqueous solutions using silicon alkoxides as precursor and ammonia as a catalyst.\textsuperscript{1} However, even after several decades the mechanism for the silica formation via the sol-gel reaction is still not well understood.\textsuperscript{2-4} The knowledge of how the silica particles are formed in the nanocomposites is very important because it allows a better understanding and thus control over the morphology of the \textit{in-situ} nanocomposites.\textsuperscript{5-7}

So far, two hypotheses have been proposed for the silica formation in aqueous solutions, namely monomer addition (hydrolyzed or non-hydrolyzed TEOS) and controlled aggregation. The monomer addition model proposed by Matsoukas and Gulari\textsuperscript{8,9} suggests a mechanism where, after an initial burst of nucleation, growth continues through the addition of hydrolyzed silica intermediates on the particle surface. The monodispersity of the size distribution of the silica particles was then explained via a so-called ‘self-sharpening’ mechanism, assuming that smaller particles grow faster than the bigger ones.\textsuperscript{10,11} The controlled aggregation model suggested by Bogush and Zukoski\textsuperscript{12-14} suggests a continuous nucleation throughout the reaction and aggregation of primary particles or nuclei yielding the final silica particles. Van Blaaderen\textsuperscript{11} suggested that both mechanisms, i.e. monomer addition and controlled aggregation are responsible for the silica formation during the sol-gel reaction where initially silica particles are formed via aggregation and further growth continues by addition of small hydrolyzed silica intermediates.

Another approach for the formation of silica nanoparticles via the sol-gel reaction is the use of inverse emulsions in non-aqueous solvents, commonly called water-in-oil emulsions.\textsuperscript{15} An emulsion is a mixture of two or more immiscible liquids in the presence of a surfactant. An inverse emulsion is obtained when polar water droplets are dispersed in a non-polar phase and stabilized by a surfactant.\textsuperscript{16-18} Surfactants are organic compounds that are amphiphilic in nature because their chemical structure consists of a hydrophilic and a hydrophobic part that allows the surfactant to remain on the interface between the polar and the non-polar phase.
The particular arrangement of the surfactant at the water-oil interface above a certain concentration, called the critical micelle concentration (CMC)\(^{19,20}\) leads to the formation of micelles. The shape and the size of the micelle is a function of the molecular geometry of the surfactant molecules and the surfactant concentration, temperature, pH, and ionic strength.\(^{21-24}\) Two types of micelles can be distinguished, normal micelles where the polar group of the surfactant is facing the polar phase and the non-polar part facing the centre of the micelle (e.g. oil-in-water emulsions) and inverse micelles where the polar groups are arranged on the water interface pointing towards the centre of the micelle and the non-polar part is facing the non-polar phase (e.g. water-in-oil emulsion)\(^{25-27}\)

The inverse emulsion is of particular interest for our study due to the possibility to synthesize a variety of inorganic particles (SiO\(_2\), TiO\(_2\) and ZrO\(_2\)) with well-controlled size using the sol-gel method.\(^{28-32}\) The main advantage of the emulsion process is that it enables a better controlled microstructure and size of the silica particles. The particle size is influenced by the water-to-surfactant ratio \(R\), where for a higher ratio i.e. above 1, the inverse micelle consists of bound and free water resulting in larger size particles and for a smaller ratio, i.e. below 1, the opposite is valid. In the latter case the water in the micelle is mostly bounded, thus with a limited mobility, resulting in a retardation of the TEOS hydrolysis and condensation reactions leading to smaller particle sizes.\(^{33}\)

So far, the mechanism for silica formation via sol-gel reaction has been studied only in aqueous solutions using techniques such as small-angle X-ray scattering (SAXS)\(^{34-37}\) and liquid NMR.\(^{38-41}\) In this chapter, for the first time, an attempt is made to study the mechanism of silica formation directly in the rubber matrix. Real-time SAXS and \(^1\)H-MAS NMR measurements were performed on rubbers to gain additional insight into the kinetics of the sol-gel reaction and possibly the silica intermediates. In addition, the possibility to perform sol-gel reactions in a rubbery material (NR and EPDM) at higher temperatures up to 120 °C will be demonstrated in order to explore future industrial applications of this process, such as reactive extrusion.
3.2. Experimental section

3.2.1. Materials

The silica precursor, TEOS and the (n-hexylamine) catalyst were purchased from Aldrich and used as received. The characteristics of the two rubbers, namely natural rubber (NR; Tun Abdul Razak Research Centre) and ethylene-propylene-diene rubber (EPDM; Lanxess), are shown in Table 3.1.

Table 3.1 Characteristics of rubber materials used.

<table>
<thead>
<tr>
<th>Rubber type</th>
<th>NR</th>
<th>EPDM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SMR L</td>
<td>Keltan 512</td>
</tr>
<tr>
<td>Composition [wt%]</td>
<td>Isoprene (1,4-cis)</td>
<td>Ethylene/Propylene/ENB (55/41/4.3)</td>
</tr>
<tr>
<td>Impurity [wt%]</td>
<td>0.5</td>
<td>/</td>
</tr>
<tr>
<td>$M_w$ [kg/mol]</td>
<td>~800</td>
<td>260</td>
</tr>
<tr>
<td>Mooney viscosity</td>
<td>50-60 (100°C)</td>
<td>46 (125°C)</td>
</tr>
<tr>
<td>ML (1+4)</td>
<td>50-60</td>
<td>46</td>
</tr>
<tr>
<td>Tg [°C]</td>
<td>-65</td>
<td>-54</td>
</tr>
</tbody>
</table>

It was difficult to determine the exact molecular weight of the NR using gel permeation chromatography (GPC), because there was always residual gel. Literature suggests an approximate $M_w$ value of $8 \times 10^5$ g/mol and $M_w/M_n = 2.3$.

3.2.2 Characterization

Solid-state NMR

Solid-state NMR spectroscopy is used to follow the kinetics of the sol-gel reaction directly inside the rubber matrix at different temperatures. The NMR measurements were performed in collaboration with Dr. M. R. Hansen and C. at the Max Planck Institute for Polymer Research in Mainz, Germany. Single-pulse $^1$H magic-angle spinning (MAS) NMR spectra were recorded on a Bruker Avance I spectrometer with a Larmor frequency of 700.25 MHz for $^1$H by using a 4.0 mm probe.

Sample preparation: The sol-gel reactions were performed in small capillaries
(Pyrex MAS Rotor Insert by Wilmad LabGlass) with a diameter of 2 mm, fitting exactly in a 4.0 mm rotor. 2.5 mg of the natural rubber compound was placed in the capillary and swollen with 2.5 µl tetrathoxysilane (TEOS, with 1% chromium acetylacetonate as relaxation agent) in an oven at 80 °C. After 30 min, the swelling of 50 wt% was completed and the catalyst (0.096 mol/l water-catalyst solution) (TEOS: H₂O in 1:2 ratio) was injected into the glass capillary which was finally sealed by using a flame. The capillary was then placed into the rotor and the free volume on top was filled with Teflon tape to ensure stable magic angle spinning (MAS) of the rotor. The probe was preheated to the reaction temperatures of 40 °C, 60 °C, 80 °C, 100 °C and 120 °C, respectively. The rotor was placed in the probe, a MAS frequency of 5.0 kHz was applied after temperature equilibration and the acquisition of data during the reaction was started. The whole process of sealing the capillary until the start of the acquisition took up to 5 min. For the experiments a dwell time of 40.0 µs was used. For every minute 16 spectra with a repeating time of 1 s were recorded and averaged to form one spectrum. Depending on the reaction speed the total recording time was between 64 and 1024 min.

**Single pulse measurements (²⁹Si MAS):** The single pulse measurements were performed for quantitative determination of the silica structure (Q⁴, Q³ and Q²). The single-pulse ²⁹Si MAS experiments were carried out on a Bruker Avance I spectrometer operating at a Larmor frequency of 700.25 MHz and 139.12 MHz for ¹H and for ²⁹Si, respectively, using a 4.0 mm probe. A MAS frequency of 10.0 kHz and proton decoupling (TPPM) were used to remove anisotropic interactions. In all experiments a relaxation delay of 10 s and a radio frequency power of 50.0 kHz were used corresponding to a 5.0 µs 90 degree pulse. The in-situ nanocomposites used for the single pulse measurements were prepared in advance as follow: the rubber samples with dimensions (10 x 10 x 1 mm³) were swollen in TEOS until an amount of 50 wt% was achieved followed by immersion in the catalyst solution at 100 °C for 15 and 60 min. The sol-gel reaction was stopped by fast immersion of the material in liquid nitrogen. The frozen samples were transferred into a Christ Alpha 2 - 4 freeze dryer, operated at 0.2 mbar for 2 days at 20 °C, for fast removal of the organics and minimizing the possibility for the sol-gel reaction to continue
during the drying process.

**Dynamic light scattering (DLS)**

The average diameter of the inverse micelles was measured with Malvern Zetasizer Nano ZS dynamic light scattering apparatus with a He-Ne laser as the light source (wavelength of 632.8 nm). This apparatus was used at a scattering angle of 173 ° and a temperature of 25 °C. DLS measures the Brownian motion of the particles assuming they are spherical in shape and relates this to the size of the particles. The larger the particle, the slower the Brownian motion will be. In order to estimate the size of the inverse micelles we used a model system based on toluene to mimic the non-polar nature of the rubber. The toluene and water phase (0.096 mol/l catalyst solution) were kept for 2 - 3 days to allow diffusion of possible micelles from the water into the toluene phase. Prior to the measurement the toluene phase was filtrated with a 100 nm filter to remove any impurities that might influence the measurement.

**Transmission electron microscopy (TEM)**

*Cryogenic transmission electron microscopy (cryo-TEM):* measurements were performed on a FEI Tecnai 20, type Sphera TEM instrument (operating voltage of 200 kV) The sample vitrification procedure was performed using an automated vitrification robot (FEI Vitrobot Mark 3). A 3 µl sample is applied to a Quantifoil grid within the environmental chamber of the Vitrobot and the excess toluene was blotted away for 2 - 3 sec. The temperature in the Vitrobot was adjusted to 4 °C to prevent evaporation of the toluene. A thin film was formed and the sample was shot into liquid nitrogen. Liquid ethane cannot be used because toluene dissolves quite easily in ethane. The grid containing the vitrified film was immediately transferred to a cryo-holder (Gatan 626) and observed under low dose conditions at - 170 °C. It should be noted, that later in the text it will be referred to structure and not morphology of the nanocomposites.

*TEM Ultramicrotomy:* ultrathin sections (70 - 100 nm) were obtained using a Reichert-Jung Ultracut E microtome equipped with a diatome diamond knife for
dry cutting for trimming (45° angle) and sectioning (35° angle) at temperature of -140 °C. The sections were placed on 200 mesh copper grid with a carbon supportive layer. The sections were examined with the TEM Sphera instrument, FEI Tecnai 20 (operating voltage of 200 kV).

**Small-angle scattering (SAXS)**

In-situ small angle X-ray scattering (SAXS) was used to allow real-time observation of the silica growth via the sol-gel reaction in rubber as a function of time at different temperatures. The SAXS measurements were performed at beam line BM26/DUBBLE of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Time-resolved SAXS patterns were recorded with a two-dimensional gas-filled detector (512 x 512 pixels with a 260 μm pixel size) placed at 3.5 and 7 m detector-to-sample distance. The wavelength used was \( \lambda = 1.033 \) Å. Scattering and absorption from air were minimized by a vacuum chamber placed between sample and detector. SAXS images were acquired every 15 sec resulting in 240 frames during the reaction time of 60 min. Each SAXS image was corrected for the intensity of the primary beam, absorption, sample thickness and background. The background signal was recorded at \( t = 0 \) min for each separate sample before the start of the sol-gel reaction.

The non-crosslinked rubber samples (NR, EPDM and SBR) were swollen to 50 wt% TEOS (NR and SBR) and 33 wt% TEOS (EPDM) in an oven at 80 °C directly into a glass capillary (\( d = 2 \) mm). The catalyst solution with ratio TEOS/H\(_2\)O = 1:2 was injected into the capillary surrounding the sample from all sides. After the injection of the catalyst solution the capillary was sealed and immediately placed in a specially designed pre-heated pressure cell\(^{43}\) that allowed enough pressure to keep the catalyst solution in the capillary in its liquid state. A small volume of the capillary was exposed to the X-ray beam. The time between the addition of the catalyst solution in the capillary and the start of the sol-gel reaction was approximately 3 min. The reaction was performed for 60 min at three different temperatures 80, 100 and 120 °C, respectively.
Surface tension

The surface tension method provides information on the change of the surface tension of the water (CMC determination) due to the addition of a certain chemical compound and helps identifying whether this compound behaves as a surfactant. The surface tension measurements were carried out at 20 °C on a DCAT 11 tensiometer (Data Physics Instruments GmbH), employing a PT11 Wilhelmy plate made of platinum-iridium equipped with automatic liquid dosing and refill unit (LDU) for automatic dosing of the surfactant. The surfactant concentration was gradually increased up to a final concentration in the water of 4 g/l. The decrease in the surface tension of the water was followed.

Conductivity

The change in the conductivity as a function of the hexylamine concentration was followed with a PW9571/60 four-point electrode cell in combination with a PW9527 digital conductivity meter at 4000 Hz. The measurement was performed at room temperature. Initially the conductivity of pure water was measured and later the catalyst was gradually added in a glass vessel equipped with a magnetic stirrer to provide better homogenization of the solution. Between each measurement the electrode was carefully cleaned with deionised water to prevent any errors in the measurement.

Degree of swelling

The degree of swelling of the rubber in pure water and in the catalyst solution was determined by the following equation:

\[ S = \frac{M_2 - M_1}{M_1} \cdot 100 \% \]  

(3.1)

where \( M_1 \) is the initial mass of the rubber and \( M_2 \) is the mass of the swollen rubber in TEOS after 30 min swelling time.
3.3. Results and Discussion

3.3.1. Chemistry of silica formation via sol-gel reaction

The sol-gel reaction under either acid- or base-catalyzed conditions proceeds in two steps: 1) hydrolysis and 2) condensation. In our case the reaction is performed under basic conditions using hexylamine as catalyst. So far the sol-gel reaction was performed in aqueous solutions under basic conditions in presence of ammonia, as initially proposed by Stöber in 1968. In order to synthesize the silica particles directly inside the rubber matrix, a certain amount of the ammonia catalyst needs to diffuse into the non-polar rubber phase to initiate the silica formation. However, due to the large difference in polarity between the ammonia solution and the rubber it is expected that the diffusion in the rubber is strongly retarded, resulting in lower silica content in the obtained nanocomposite and preferred concentration of the formed silica on the surface of the nanocomposite. Therefore, a different type of catalyst was used, namely hexylamine, consisting of a polar amino group and a non-polar alkyl chain (amphiphilic molecule), that is expected to have a stronger affinity towards the rubber matrix and to lead to a higher final silica content. Aliphatic amines are derivatives of the ammonia obtained by substitution of the hydrogen atoms with alkyl groups. It is well known that the alkyl groups elevate the basicity of the amines which generally increases with the number of alkyl groups substituted. Hexylamine is a stronger base than ammonia as reflected by its $P_k$ value, and therefore a higher concentration of hydroxyl ions will be obtained during the hydrolysis reaction, which together with the amphiphilic properties makes hexylamine the preferred choice of catalyst for the sol-gel reaction in the rubber matrix (NR and EPDM). The combination of good basicity and amphiphilic properties of the hexylamine leads to in-situ nanocomposites with higher silica content as already shown by Ikeda et al. The silica formation under basic conditions proceeds via an ionic mechanism where the hydroxyl ions are used to start the hydrolysis and the condensation reaction, as shown in Figure 3.1.
Chapter 3

Hydrolysis: (2) and (3) silica intermediates

Condensation: a) (1), (2) or (3) + OH\(^-\) \(\Rightarrow\) remove CH\(_3\)CH\(_2\)OH (or H\(_2\)O) \(\Rightarrow\) ionic intermediates (4) and (5)

b) (4) or (5) + (1-red), (2-red) or (3-red) \(\Rightarrow\) (6) and (7) \(\Rightarrow\) remove CH\(_3\)CH\(_2\)OH (or H\(_2\)O) \(\Rightarrow\) (8) and (9)

Figure 3.1. Chemistry of silica formation under basic conditions via an anionic mechanism.

The hydrolysis begins with the exchange of the ethoxy groups from the TEOS molecule with hydroxyl ions, leading to formation of several partially hydrolyzed TEOS intermediates such as: Si (OEt)\(_3\)(OH) (2), Si (OEt)\(_2\)(OH)\(_2\), Si (OEt)(OH)\(_3\)
and the fully hydrolyzed form of TEOS, the silicic acid Si(OH)$_4$ (3), when all ethoxy groups are exchanged by hydroxyl groups. The substitution of the ethoxy with hydroxyl groups results in an increase of the positive charge on the silicon atom (hydroxyl groups are strong electron withdrawing groups) increasing the reactivity of the hydrolyzed species and allowing each subsequent substitution to proceed faster. This results in an increase in the hydrolysis rate with each substituted hydroxyl group in the TEOS molecules via a so-called self-accelerating mechanism.$^{48}$

The condensation reaction is initiated by the attack of the hydroxyl ion to one of the hydrolyzed intermediates forming a negatively charged silica intermediates (4 and 5) and a leaving water or ethanol molecule. These intermediates are highly reactive and very quickly react with other molecules (indicated 1 to 3 in red) forming a penta-coordinated complex and negatively charged silica intermedaites.$^{49}$ A similar self-accelerating mechanism is present for the condensation reaction as well. The reactivity of the condensed intermediates will depend on the number of Si-O-Si bonds formed, more Si-O-Si bonds lead to a higher reactivity. Therefore, the larger silica intermediates consisting of more Si-O-Si bonds will be more reactive than the smaller ones and will preferentially consume the products from the hydrolysis reaction and grow faster into solid silica particles.$^{50}$ Since condensation may begin after the first exchange of the ethoxy with hydroxyl groups, occurring almost instantly after the hydrolysis reaction, some ethoxy groups may remain non-hydrolyzed due to steric hindrance and end-up trapped inside the silica network or on the silica surface.$^{51}$

This final step of the condensation is the cyclization reaction that begins with the formation of the smallest cyclic structure, 3-ring, and later continues to produce larger ring structures. The ring structures are favoured under stronger alkaline conditions and particularly at higher temperatures.$^{49}$ Moreover, the formation of a ring requires breakage of the intra-molecular hydrogen bonding in the linear silica intermediates.$^{52-54}$ The presence of remnant ethoxy groups in the linear species may lead to formation of less hydrogen bonding which can allow easier re-structuring of the linear intermediates into a ring structure and in this way promote the cyclization
reaction leading eventually to formation of 3D silica structure.

The reaction path of the sol-gel chemistry schematically presented in Figure 3.1 has been documented in literature, but the role of hexylamine during the sol-gel reaction and particularly its interaction with the growing silica intermediates formed during reaction is unknown.

An attempt was made to explain the possible role of the cations during the silica formation via a simulation study. The study was conducted under basic conditions in the presence of two positively charged ions NH$_4^+$ and Li$^+$. The cations may affect the organization of the water molecules involved in the silica condensation and increase the barrier for Si-O-Si formation due to charge stabilization of the negatively charged silica intermediates. Moreover, the effect of the cation is strongly dependent on its size and nature. In our case, hexylamine is a relatively large molecule and its involvement in the silica formation is not very clear at this moment. It is possible that it initially interacts with the negative charges on the silica species via electrostatic interactions and in the later stages due to the decrease of these negative charges (consumed in the silica growth) starts interacting with the silanol groups via hydrogen bonding. Further elaboration on the possible interactions between the hexylamine and the silica surface will be presented in Chapter 4.

3.3.2. Mechanism of in-situ silica formation in rubber via sol-gel reaction

Ikeda et al. were the first to propose the hypothesis according to which the sol-gel reaction in the TEOS-swollen rubber proceeds via the formation of inverse micelles stabilized by hexylamine, in which hexylamine behaves not only as a surfactant but also as catalyst. Unfortunately, no evidence was provided to support this hypothesis. In order to explore the possibilities of this hypothesis, one must begin by determining whether hexylamine has the potential to behave as surfactant. Therefore, the surface tension and the conductivity were measured as a function of hexylamine concentration. The results are shown in Figure 3.2.
Figure 3.2: (a) Surface tension and (b) conductivity of hexylamine-water solution as a function of hexylamine concentration.

Figure 3.2 shows initially a steep decrease of the surface tension of the water by the addition of hexylamine (Figure 3.2 (a)) indicating indeed that hexylamine acts also as a surfactant. At approximately - 1.25 g/l concentration of hexylamine the curve shows a weak shoulder. The origin of this shoulder is not quite clear at the moment, however, it might be a result of possible re-organization of the hexylamine molecules. After a certain concentration a plateau is reached that corresponds to the so-called critical micelle concentration (CMC). The CMC of the hexylamine, was determined from the intercept of the two straight lines for both measurements (surface tension and conductivity) and showed a CMC value of 0.323 g/l.

The conductivity measurement revealed the existence of charged micelles where a clear increase in conductivity with increasing hexylamine concentration was observed. Ions in the solution can certainly be expected because hexylamine is a relatively strong base which deprotonates the water by accepting a proton and forming OH- ions.

For preparing the in-situ nanocomposites the used concentration of the hexylamine in the catalyst solution was always 9 g/l (0.096 mol/l) which is close to the maximum solubility of hexylamine in water. Clearly, this value is much higher than the obtained value of the CMC = 0.323 g/l and it can be said that at the concentration hexylamine is used in the sol-gel reaction it indeed forms charged micelles in the water. Upon diffusion of the catalyst solution in the TEOS swollen
rubber, most probably the micelles convert into inverse micelles in order to allow
easier penetration of the water into the apolar rubber matrix. Direct observation of
these inverse micelles in the rubber is extremely difficult with TEM due to their small size\textsuperscript{57} and the weak electron density contrast between the rubber matrix and
the water (and hexylamine).\textsuperscript{58}

It is believed that the inverse micelles shield the polar water in their interior, by
positioning the non-polar alkyl chains of the hexylamine on the outer side of the
micelles, thus facilitating easier diffusion into the non-polar rubber phase. To check
this, the uptake of water and catalyst solution was measured by the NR matrix
(no TEOS), expressed in terms of swelling degree, as shown Figure 3.3.

![Figure 3.3. Absorption of pure water and water-catalyst solution in NR at 80 °C as a function of swelling time.](image)

The results in Figure 3.3 indicate indeed faster of water in the presence of
hexylamine (11 % swelling degree) as compared to the absorption of pure water
(3% swelling degree) in the rubber. This means that hexylamine indeed promotes
water diffusion inside the rubber matrix possibly via the formation of inverse
micelles. Therefore we assume that the preparation of the \textit{in-situ} nanosilica
particles via a sol-gel reaction in the rubber matrix proceeds via the mechanism, as
shown schematically in Figure 3.4.
The process of silica formation starts with the swelling of the rubber with the silica precursor (TEOS) and immersion of the swollen rubber into the catalyst solution at a certain temperature $T$ and reaction time $t$, determined by the amount of silica required in the final in-situ nanocomposite. The inverse micelles are expected to act as small nano-reactors hosting the sol-gel reaction for the silica formation. Due to the similar apolar nature of TEOS and hexylamine (based on the Hildebrand parameters, 16.4 and 16.2 MPa$^{1/2}$ for TEOS and hexylamine, respectively) TEOS should diffuse easily through the alkyl chains of the hexylamine and reach the micelle interface where hydrolysis starts. The hydrolysis of the TEOS is initiated by the hydroxyl ions present in the water phase, via the exchange of the ethoxy groups (see Figure 3.1). The partially hydrolyzed TEOS will have a higher polarity than the pure TEOS due to the presence of the hydroxyl groups. As the hydrolysis proceeds further, more ethoxy groups from the TEOS are converted leading to further increase in polarity of the hydrolyzed TEOS. This eventually leads to migration towards the interior of the inverse micelle where condensation preferably continues until solid silica particles are formed.

In general, the inverse micelles are dynamic systems with tendency to interchange and coalesce during the emulsion process. This is determined from the nature of the surfactant which provides electrostatic or steric stabilization to the inverse micelles. However, in our case the degree of interchange and coalescence between the inverse micelles in the rubber is expected to be additionally restricted.
by the rubber chains that significantly impart micelle mobility. It is expected the hexylamine to provide good stabilization due to the ionic interactions existing on the interface between the polar amino group of the hexylamine and the water in the micelle. The ethanol produced during the reaction, is expected initially to migrate towards the water in the interior of the micelle due to its polar nature. In the later stages of the reaction as silica particles grow and become denser, it can be pushed outwards in the rubber phase.

In order to provide further evidence for the existence of the inverse micelles in the rubber matrix, a model system using toluene (with similar apolar nature) was prepared to mimic the rubber matrix. The model system is prepared in such a way that the toluene and the catalyst solution were added together and left for 2 - 3 days at room temperature to allow diffusion of the micelles from the catalyst solution into the toluene phase. As mentioned above, these micelles are expected to convert into inverse micelles enclosing water with the hexylamine residing on the interface, as shown schematically in Figure 3.5 (a).

![Figure 3.5. (a) Schematic drawing of the toluene model system and (b) size of the inverse micelles inside the toluene phase as determined by dynamic light scattering (DLS).](image)

The toluene phase was extracted and DLS measurements were performed in order to detect possible inverse micelles. The DLS measurement revealed structures in size range of 5 - 10 nm (as indicated with the lines in Figure 3.5 (b)) that can be
attributed to inverse micelles. An attempt is made to observe the inverse micelles also with cryo-TEM by preparing thin films of toluene with the Vitrobot under cryo-conditions (described in section 3.2.3.). However, the TEM images could not reveal anything conclusive, possibly due to the low electron density contrast of the water and the toluene at cryo-conditions (-170 °C). In a next step to confirm the presence of inverse micelles, TEOS was added only to the toluene phase (see Figure 3.6) and allowed the system to react for 60 min at 40 °C for possible silica formation.

Figure 3.6. Schematic representation of formation of silica particles via sol-gel reaction via a model system using toluene to mimic rubber matrix.

Figure 3.6 showed that indeed the sol-gel reaction occurred in the toluene phase and silica particles and aggregated structures are formed as can be observed in the TEM image. This can be used as an additional evidence for the existence of inverse micelles in the toluene phase, because the sol-gel reaction cannot proceed in the absence of water. The most probable way the water enter the toluene phase is via the inverse micelles and not via spontaneous emulsification,\textsuperscript{59} because of the very low solubility of toluene in water (approximately 0.051 %).\textsuperscript{60} The TEM image in Figure 3.6 shows that both individual particles and aggregates are formed in the TEOS-toluene-catalyst solution system. In order to confirm the nature of these aggregates, an elemental analysis was performed with TEM-EDX through the whole grid, and the results from this analysis are shown in Figure 3.7.
Figure 3.7. Elemental analysis performed by TEM-EDX on (a) area of TEM copper (Cu) grid and (b) silica aggregate extracted from toluene phase.

For the TEM-EDX an aggregate was selected because it was very difficult to focus on one single particle. Two positions are identified in Figure 3.7, i.e. position 1 that corresponds to the area in the near vicinity of the aggregate (the grid) and position 2 which is located on the aggregate itself. The results from position 1 (see Figure 3.7 (a)) clearly show strong signals from the carbon (C) and the copper (Cu) that are the building elements of the TEM grid (Cu mesh coated on one side with carbon film). The low intensity peaks corresponding to oxygen (O) and silicon (Si) probably originate from the remnant TEOS present on the grid. The peaks in position 2 clearly suggest that the aggregate structure is composed of silica particles, as indicated by the very strong peaks of the silicon (Si) and the oxygen (O) assigned to the Si-O-Si network in the formed silica (see Figure 3.7 (b)).

Interestingly, an increase in the C peak is also observed, indicating the possible presence of the ethoxy groups or alkyl chains of the hexylamine inside or on the surface of the silica particles.

It is well known from emulsion polymerization processes\textsuperscript{30,61} that the surfactant molecules usually remain on the particle surface and are removed after a thermal treatment (calcination) at 400 °C. However, in the functionalization of the inorganic particles this is considered beneficial because it converts the usually hydrophilic surface into a more hydrophobic one via the process of inverse emulsion.\textsuperscript{62} In analogy, it is expected the hexylamine as surfactant to remain on the
surface and contribute to the hydrophobic character of the silica. The objective in this section was to investigate how the silica nanoparticles are formed in the rubber matrix when using hexylamine as catalyst. The results showed that hexylamine can also behave as surfactant, thus forming inverse micelles which are used as nano-reactors hosting the sol-gel reaction for silica formation. The sol-gel reaction via inverse emulsion might be considered as a unique way to prepare in-situ nanocomposites, combining in one step excellent silica dispersion and surface functionalization.

3.3.3. Kinetics of sol-gel reaction as determined by time-resolved solid-state NMR

Many efforts have been made to understand the reaction mechanism of the sol-gel reaction.\textsuperscript{63,64}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{schematics.png}
\caption{(a) Assignments of the $Q^1$, $Q^2$ and $Q^4$ peaks (b) reaction steps of the sol-gel reaction. Every single grey arrow stands for a specific reaction rate constant. Quaternary silicon tetrahedra are symbolized by $^\varepsilon Q^\eta \sigma$. $\varepsilon$, $\sigma$, and $\eta$ are the numbers of ethoxy groups (-OEt), siloxane bonds (-OSi) and hydroxy groups (-OH), respectively.}
\end{figure}

Figure 3.8 shows a schematic representation of the possible reaction steps of the sol-gel reaction occurring during the transformation of the liquid TEOS into a solid particle showing that there are many reaction pathways possible until a certain condensation degree of the silica is reached. The reaction rates of each particular
pathway can vary as a result of steric and mobility hindrance of the silica intermediates formed along the condensation reaction. This results in a non-linear time-dependent behaviour of the sol-gel reaction in the rubber matrix, thus no rate constants were obtained. Therefore, the complexity of the sol-gel reaction prevents obtaining one reaction rate and, although much progress has been made in this field, the precise reaction kinetics of the silica formation still remains unclear.

It has to be noted that, up to now the kinetics of the sol-gel reaction has only been studied in aqueous solutions. In this study, an attempt is made to determine the reaction kinetics directly in the rubber matrix as a function of different temperatures (40 - 120 °C) by using the proton ($^1$H) NMR spectroscopy. The sol-gel process in the rubber was performed in a specially designed capillary filled with TEOS-swollen rubber and catalyst solution, placed in the NMR rotor as described in Section 3.2.2. Both liquid and solid-state NMR signals were probed and the results are shown in Figure 3.9.

![Figure 3.9. Comparison of the $^1$H NMR spectra performed in the liquid-state at 7.05 T (dashed line) and in the solid-state at 16.45 T using a HR-MAS probe and 5.0 kHz spinning frequency.](image)

The two $^1$H NMR spectra in Figure 3.9 clearly show the enhancement in resolution using the solid-state $^1$H-MAS NMR technique as compared to the solution $^1$H NMR
spectroscopy. The NR matrix in the reaction system leads to broad resonances that cannot be averaged out by the common spinning frequency of 20 - 30 Hz in solution NMR. In contrast $^1$H-MAS at a moderate MAS spinning frequency of 5.0 kHz is eligible to provide sharp resonance lines, which can be analyzed quantitatively. The decrease of the ethoxy groups (TEOS) and the increase in the ethanol peak during the sol-gel reaction was used to follow the kinetics, as shown in Figure 3.10.

![Figure 3.10. 2D reaction profiles of sol-gel reaction in NR as followed by $^1$H-MAS NMR showing decrease of ethoxy groups (TEOS) and increase of ethanol. See Figure 3.9 for colour assignments of the peaks.](image)

The position of the characteristic protons in the TEOS (ethoxy groups), in the ethanol and in the NR are indicated with the coloured circles shown in the 2D reaction profile in Figure 3.10. The decrease in TEOS amount during the sol-gel reaction occurs as a result of the hydrolysis and condensation reaction during which the ethoxy groups become hydrolyzed and incorporated in the growing silica intermediates building the silica structure. This might result in their complete immobilization which makes them non-detectable by NMR. Thus, one is able to follow the ethoxy groups from the TEOS as long as the TEOS is mobile enough. In the remainder of this chapter the TEOS molecules will be termed ethoxy groups as being the more chemically correct term. Consequently, the amount of ethanol...
produced during each reaction pathway (see Figure 3.8) results in an increase of the intensity of the ethanol peak with time. The increase in the ethanol peak and the decrease in the TEOS peak reach a plateau, after a certain reaction time when no ethanol is formed and no TEOS is consumed anymore. This indicates the end of the sol-gel reaction in rubber and thus of the silica formation.

The resonances of the NR at 1.63 ppm (CH$_3$) and 2.01 ppm (CH$_2$) are clearly separated from the signals of both the ethanol and ethoxy groups. Ethanol shows signals at 1.16 ppm (CH$_3$) and 3.62 ppm (O-CH$_2$) and the ethoxy groups at 1.14 ppm (CH$_3$) and 3.73 ppm (O-CH$_2$). The O-CH$_2$ signals can be distinguished well enough for a quantitative analysis, while the CH$_3$ resonances of ethanol and ethoxy are too close to each other to be de-convoluted. The spectra were fitted with a MATLAB algorithm to give the relative intensities of the O-CH$_2$ signals of the ethanol, the ethoxy groups and the intensity of the CH$_2$ signal of the NR. Since the signals of the NR do not change during the reaction, they are used as internal standard for the normalization of the peak intensities of the ethanol and the ethoxy according to the equation:

$$n_i = \frac{I_i \cdot N_{NR}}{N_i \cdot I_{NR}} \cdot n_{NR}$$

where $n_i$ are the moles of the ethanol and the ethoxy groups calculated from the peak intensities, $I_i$ and $I_{NR}$ are the peak intensities of the ethoxy groups (and ethanol) and the NR, $N_i$ is the number of protons in the ethoxy groups and the ethanol, two protons for each originating from the O-CH$_2$ group, $N_{NR}$ is the number of protons for the NR, thus four protons (CH$_2$-CH$_2$) and the $n_{NR}$ is the amount of NR in $\mu$mol which was constant in all experiments. The absolute amounts of ethoxy and ethanol, in $\mu$mol, were calculated from eq. 3.2 at each reaction temperature. The obtained reaction curves at different temperatures in Figure 3.11 show the time dependent progression of the amount of (a) the ethoxy groups and (b) the ethanol.
Figure 3.11. Time-dependent progression of the amounts of (a) the ethoxy groups and (b) the ethanol at 40, 60, 80, 100 and 120 °C as recorded by $^1$H HR-MAS NMR during silica formation via sol-gel reaction in the rubber matrix.

From Figure 3.11 it can be seen how the absolute amount [μmol] of the ethoxy group and of the ethanol changes with time at each temperature. As observed in Figure 3.11 (b), the final ethanol content (the plateau level) is not the same at higher temperatures (> 80 °C) as compared to the plateau at lower temperatures.

This can be ascribed to the loss of signal intensity from the ethanol during the NMR measurement because above 80 °C the ethanol starts to evaporate. It is known that the relaxation time of the gas molecules can be much longer as compared to the same molecules in a liquid. The repeating time of 1 s is therefore not enough for the gaseous ethanol molecules to relax to their initial magnetic equilibrium state which eventually results in loss of signal intensity.

This means that the signal of the gas molecules cannot be measured during the reaction, and will decrease with increase in temperature. It is obvious that the end-reaction time which corresponds to the time needed for the ethanol and the ethoxy groups to reach a plateau, is strongly dependent on temperature. Higher reaction temperatures resulted in a significant increase in the reaction rate, thus a shorter time to reach a plateau as shown in Figure 3.12 (a).
Figure 3.12. (a) Time for ethanol to reach a plateau value as function of temperature, (b) ethanol formation as a function of temperature for three different reaction times (15, 30 and 60 min).

Figure 3.12 (a) shows that the time needed for the ethanol to reach a plateau decreased with increasing the reaction temperature from approximately 400 min at 60 °C to only 40 min at 120 °C. A 10 fold decrease in reaction time with the temperature suggests that the reaction rate accelerates strongly with increasing reaction temperature. This result is important, particularly when silica formation needs to be done on an industrial scale via reactive extrusion, where high temperatures and very short reaction times are required. Due to the non-linear behaviour of the sol-gel reaction in rubber the data were not compliant to the standard Arrhenius analysis and the activation energies were not obtained. Another comparison between the reaction kinetics at different temperatures can be done by following the ethanol formation (normalized to the plateau value). In Figure 3.12 (b) the results of this comparison at 15, 30 and 60 min reaction time are shown. The ethanol content produced from the hydrolysis and condensation reaction during the silica formation increases with the reaction temperature at equal reaction time. The conversion of TEOS during the sol-gel reaction can be estimated using the following equation:
where, \( Wt\%_{\text{Experimental silica}} \) is the amount of silica determined from the TGA at the end of the reaction and the \( Wt\%_{\text{Theoretical silica}} \) is the theoretical amount of silica (22.3 wt% for 50 wt% TEOS) calculated from the stoichiometric ratio of TEOS and \( \text{SiO}_2 \) where 1 mol of TEOS corresponds to 1 mol of formed silica (\( \text{SiO}_2 \)) as shown in the following equation:

\[
\text{Si} \,(\text{OC}_2\text{H}_5)_4 + 2\text{H}_2\text{O} \Rightarrow \text{SiO}_2 + 4\text{C}_2\text{H}_5\text{OH} \quad (3.4)
\]

The amount of the produced silica measured with TGA after the NMR measurements and the TEOS conversion at different reaction temperatures are shown in Table 3.2.

Table 3.2. Conversion of the ethoxy groups (TEOS) during the sol-gel reaction in NR nanocomposite as determined by \(^1\text{H} \text{HR-MAS NMR.}

<table>
<thead>
<tr>
<th>( T ) [°C]</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Wt%_{\text{silica}} ) [wt%]</td>
<td>19.4</td>
<td>20.6</td>
<td>14</td>
<td>12.8</td>
</tr>
<tr>
<td>TEOS conversion [%]</td>
<td>87.1</td>
<td>92.3</td>
<td>63</td>
<td>57.5</td>
</tr>
</tbody>
</table>

The amount of silica produced at lower temperatures (60 and 80 °C) is high and close to the theoretically possible silica production (TEOS conversion is close to 90 %). For the higher reaction temperatures the amount of silica is less. This is probably due to the partial evaporation of the TEOS and/or the catalyst at these high temperatures (in the capillary).

Next to the kinetics of silica formation, as a next step, the quality of the silica produced during different reaction times was determined. However, on-line recording of \(^{29}\text{Si} \) NMR spectra in order to follow the development of the silica structure is extremely difficult, due to the long relaxation times of the silicon. Therefore, two nanocomposites were prepared ex-situ under same reaction conditions (\( T = 100 \) °C, same TEOS/catalyst ratio), varying only the reaction time. A short reaction time of 15 min and a longer time of 60 min were chosen in order
to probe the possible intermediate silica products of the sol-gel reaction. For that purpose samples were prepared by freeze-drying as described in Section 3.2.2. The quantitative single-pulse $^{29}\text{Si}$ MAS NMR spectra of the prepared in-situ NR nanocomposites after (a) 15 min and (b) 60 min reaction time are shown in Figure 3.13.

![Figure 3.13. Single-pulse $^{29}\text{Si}$ MAS NMR spectra of NR nanocomposite after (a) 15 min and (b) 60 min reaction time.](image)

Figure 3.13 shows the quality of the silica in the corresponding in-situ NR nanocomposites, expressed with the ratio of Q$^3$:Q$^4$. The higher the value of Q$^4$ the more perfect is the silica structure. It is difficult to resolve well the Q$^2$ peak (91.7 ppm) due to the low intensity and the large amount of noise. The quantitative silicon spectra resulted in a Q$^3$:Q$^4$ ratio of 34:66 for the 15 min sample and 33:67 for the 60 min sample. Interestingly, even though higher degree of condensation was expected for the sample prepared at 60 min, the quantitative spectra revealed no significant difference in the silica composition for the selected reaction times. The TGA measurement resulted in increase of the silica content from 10.5 wt% for reaction time of 15 min to 17.6 wt% for 60 min reaction. Moreover, a particle size increase was observed with increase of reaction time from 20 ± 3 nm for 15 min to 30 ± 2 nm for 60 min reaction time (see Figure 3.17). This indicates that silica particles during growth change in size but not significantly in chemical structure.

In conclusion, it is interesting that relatively good quality silica particles were formed in-situ (with quality similar to that of the HD silica Q$^3$:Q$^4$ = 23:75) for only 15 min reaction time, and that Q$^3$:Q$^4$ remained almost the same as the reaction
proceeded further. The results in this paragraph suggest a significant increase (up to 10 fold) of the kinetics of the sol-gel reaction with increase in reaction temperature. The silica obtained via the sol-gel reaction showed remarkable good quality ($Q^3:Q^4$) after only 15 min reaction time (at 100 °C).

This result is very important because it indicates the possibility of performing the sol-gel reaction in rubber via industrial route such as reactive extrusion ($T$ up to ~ 150 °C and reaction time 1 - 5 min) and at the same time obtaining good quality silica.

3.3.4. Silica formation in the rubber matrix via the sol-gel reaction as followed with real-time SAXS

For the first time an attempt is made to follow the growth of the silica particles directly in the rubber matrix using real time SAXS measurements. The goal of this study is to obtain information on the development of the silica particle size with time in two different rubber matrices. Thus EPDM and NR matrices were used at three different temperatures, i.e. 80, 100 and 120 °C during the SAXS measurement. The increase in intensity with reaction time may be due to the densification of the silica particles or increase in particle number during the sol-gel reaction. SAXS covers the intensity of the scattered X-rays at small angles and is used to study particle sizes between 5 - 100 nm depending on the detector-to-sample distance. In our case two distances, 3.5 and 7 m, were used that enabled study of particle sizes in the range of 5 - 50 nm. For this kind of system synchrotron radiation is necessary because it provides a more intense monochromatic X-ray beam that allow studies of low density objects (growing silica) in the early stages of formation.$^{66,67}$

3.3.4.1 SAXS analysis

The X-ray scattering intensity is experimentally determined as a function of the scattering vector $q$ which is defined as follow:

$$q = \frac{4\pi}{\lambda} \sin \theta$$  \hspace{1cm} (3.5)
where $\lambda$ is the wavelength of the radiation and $2\theta$ is the scattering angle. The scattering profile is measured between two extremes, $q_{\text{min}}$ and $q_{\text{max}}$ between which, in general, two regimes can be established: the Porod power law regime and the Guinier regime. The Porod regime occurs at higher $q$-values (usually between $0.5 < q < 2 \text{ nm}^{-1}$), while the Guinier region occurs at low $q$-values (usually $q < 0.3 \text{nm}^{-1}$). The Porod regime gives information for the surface structure of the particle$^{67}$ where $I(q)$ and $q$ follow a power-law relationship expressed as:

$$I(q) \sim q^{-\alpha}$$  \hspace{1cm} (3.6)

where the exponent $\alpha$ has non-integer values between 1 and 4 which defines the sharpness of the interface between the silica and the rubber matrix. Information for the particle size can be derived from the Guinier regime. The radius of gyration $R_g$ can be determined from the slope of the linear dependence between $I(q)$ and $q^2$ in the so-called Guinier plot (Guinier 1939). For spherical particles the relationship between $R_g$ and the intensity is given by eq. 3.7$^{68}$

$$I(q) = I_0 \exp \left( -\frac{R_g^2}{3} q^2 \right)$$ \hspace{1cm} (3.7)

$$R_g^2 = \frac{3}{5} R^2$$ \hspace{1cm} (3.8)

where $I_0$ is the intensity at $q = 0$. It should be noted that for spherical particles the $q$-range over which the Guinier approximation is valid is $qR_g < 1.3$.$^{69,70}$ Therefore this analysis to obtain $R_g$ can use only a limited $q$-range, which usually lacks enough points for a good fit.

For this reason another approach was considered in order to obtain the values for the radius of gyration $R_g$, namely using the pair distribution function (PDF) $P(r)$. The main advantage of the PDF is that it provides a more reliable value for the $R_g$ because it takes into account the whole curve and is not limited to a small $q$ region. The shape of the PDF can also give an indication for the shape of the particles, as spherical particles give a bell-shaped Gaussian curve. The PDF can be calculated by assuming monodispersed particles with no inter-particle interactions.$^{71,66}$
In theory the calculation of $P(r)$ from the intensity is simple, however, $I(q)$ is only known over the experimental $q$-range $[q_{\text{min}}, q_{\text{max}}]$ and calculation of the Fourier transform of sometimes incomplete and noisy data (especially at $q$-range in the vicinity of $q_{\text{min}}$ and $q_{\text{max}}$) requires (hazardous) extrapolation to lower and higher angles. A solution for this could be the indirect Fourier Transform, first proposed by Glatter in 1977 and now commonly used in SAXS software’s to calculate $P(r)$. The basic hypothesis is that the particles have a finite size $D_{\text{max}}$, therefore:

$$I(q) = 4\pi \int_0^{D_{\text{max}}} P(r) \frac{\sin(qr)}{qr} dr$$  \hspace{1cm} (3.10)

In a next step $P(r)$ is parameterized on $[0, D_{\text{max}}]$ by a linear combination of orthogonal basis functions (eq. 3.10):

$$P(r) = \sum_{n=1}^{M} C_n \varphi_n (r)$$  \hspace{1cm} (3.11)

The coefficients $C_n$ are found by least-squares methods. In practice, the estimation of $D_{\text{max}}$ by the inverse Fourier transformation involves choosing multiple $D_{\text{max}}$ values and evaluation of the resulting $P(r)$ functions for their fit to the experimental scattering. The radius of gyration $R_g$ can be determined from:

$$P(r) = \frac{r^2}{2\pi^2} \int_{q_{\text{min}}}^{q_{\text{max}}} q^2 I(q) \frac{\sin(qr)}{qr} dq$$  \hspace{1cm} (3.12)

$$R_g^2 = \frac{\int_0^{D_{\text{max}}} r^2 P(r) dr}{2 \int_0^{D_{\text{max}}} P(r) dr}$$  \hspace{1cm} (3.13)
By using equation (3.7) we can calculate the average radius of particles. The scattering spectrum of the sample as a function of time (log-log) scale is shown in Figure 3.14.

![Figure 3.14](image_url)

*Figure 3.14. Log-log plot of scattering intensity as a function of scattering angle and reaction time for sol-gel reaction in NR at 100 °C.*

Figure 3.14 shows the increase in the intensity with time which is related to a change in the electron density contrast between the matrix and the newly formed particles and to a change in the total scattering volume (particle size and/or the number of silica particles). The same trend was observed for all reaction temperatures in both the *in-situ* NR and EPDM nanocomposites. The sharpness of the interface between the growing silica particle and the rubber matrix is determined by the slope at high-\(q\) (Porod region) which can vary between 1 (rough interface) and 4 (sharp interface). As shown in Figure 3.14, the slope \(\alpha\) increased from 3.2 at 5 min reaction time to 4 from 10 min and remained 4 until the end of the measurement. This can indicate that silica particles reach densification relatively fast. The size of the silica particles was determined using the pair distribution function approach. The reliability of this method was supported by the good fitting data between the model and the experimental results as shown in Figure 3.15.
Figure 3.15. Intensity vs. $q$ showing the fit between the calculated from the PDF data (solid lines) and the experimental data (symbols) for 5 and 60 min reaction time in NR and EPDM matrix at 100 °C.

The calculated pair distribution function is presented in Figure 3.16 for the NR and EPDM nanocomposites prepared at 100 °C as a function of time.

Figure 3.16. Pair distribution function ($P(r)$) of NR and EPDM at 100 °C.

The bell-shape of the $P(r)$ function shown in Figure 3.16 is usually characteristic for spherical particles. However, it has to be remarked that the $P(r)$ for NR has slightly distorted shape (more pronounced at longer reaction times). The distortion of the curve can originate from either not fully spherical particles (somewhat elongated) or particles touching each other or slightly overlapping. Since from the TEM micrographs in Figure 3.17 (c) it can be observed that the silica particles are
indeed spherical, we might assume that the curve distortion in the NR nanocomposite is due to touching or overlap of some particles.

Figure 3.17. Particle size development with reaction time at three different temperatures (80, 100 and 120 °C) for (a) NR at 100 °C and (b) EPDM, the numbers on the plot indicate the growth rate. (c) TEM images of NR and EPDM nanocomposites at 100 °C for 60 min.

Figure 3.17 presents the change in particle size with time at different temperatures. For the EPDM and NR system it can be clearly observed that at 120 °C a plateau is reached after approximately 30 min, indicating small further change in particle size with time. In the EPDM rubber the particle size at 100 °C starts to approach a plateau at approximately 60 min while at 80 °C a longer reaction time is required. The plateau at 80 and 100 °C in the NR is reached sooner (~ 30 min) than in the EPDM system. The growth rate (as determined from the slope of the linear part) in the NR changes more gradually with increase in temperature, while in the EPDM a
sudden increase is observed at 120 °C (0.78 nm/min). This can be considered as a possible threshold at which the high temperature (120 °C) promotes rather an exponential increase in the particle growth rate. As observed from Figure 3.17 the growth rate at each particular temperature losses its intensity for longer reaction times until eventually a plateau is reached and particle size does not change anymore. The reason for this behaviour can be found in the availability of the reactive intermediates, thus negative charges available for particle growth. The charge level depends on the degree of condensation which is the highest at the beginning of the silica formation, resulting in fast particle growth, and lowest towards the end, resulting in slower growth. The TEM images in Figure 3.17 (c) show an average particle size of 27 nm for EPDM while for the NR in-situ nanocomposite 30 nm is obtained with a discrepancy of approximately 2 nm from the particle size obtained from the SAXS analysis. This is an excellent match confirming further the accuracy of our method for particle size determination.

3.4. Conclusions

The complementary results from the NMR and SAXS analysis provide additional inside into the silica formation showing the changes in the silica structure (probed with NMR) and the silica size (probed with SAXS) changing with time and temperature. The increase in temperature from 40 to 120 °C resulted in a 10 fold increase in the reaction rate leading to almost complete formation of the silica particles for only 10-15 min from the beginning of the reaction. Moreover, the structure of the silica based on the $Q^3:Q^4$ ratio as obtained from the solid-state NMR measurements showed that the silica structure is almost fully formed and for longer reaction times it does not change significantly, indicating that silica particles continue to increase only in particle size. This is valuable information particularly during the reactive extrusion where silica formation proceeds under relatively short reaction times (the higher is the temperature, the shorter reaction times are expected) providing a good basis for potential use under extreme reaction conditions.
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The structure of silica nano-particles synthesized via sol-gel reaction in relation to the mechanical properties of the in-situ nanocomposites

Abstract

This chapter offers a possible explanation for the improved mechanical properties of in-situ rubber nanocomposites. These properties are strongly related to the rubber-silica interactions, as determined by the surface chemistry of the silica. The structure of the in-situ silica, mapped by MAS- NMR, indicated the presence of remnant ethoxy groups inside and on the silica surface and hexylamine residing only on the silica surface. This resulted in formation of so-called ‘hairy’ silica particles with a more hydrophobic nature. Different mechanisms responsible for the Payne effect of the in-situ nanocomposites (than commonly known for the conventional nanocomposites) are discussed in view of the obvious absence of a filler-filler network. The particular surface chemistry of the silica and morphology of the in-situ nanocomposites resulted in very high bound rubber content and excellent mechanical properties (as determined by RPA measurements).
4.1. Introduction

Commercially available silica (precipitated, fumed, etc) is an amorphous material consisting of silicon and oxygen atoms connected in a non-regular 3D network of Si-O-Si bonds with silanol groups (Si-OH) present inside the structure and on the surface. The chemical composition and the physical properties such as pore size, surface area, density and number of silanol groups are largely responsible for the utility of this material in various applications such as catalysis, separations operations and composite materials. The silanol groups are considered responsible for the high polarity of the silica.\textsuperscript{1,2,3} The distance and the arrangement of the silanol groups on the silica surface can differ depending on the production route, but in general three different types of silanol groups can be distinguished: isolated silanols that have only one OH group not hydrogen-bonded to neighbouring silanols, vicinal silanols that contains hydroxyl groups close enough to develop hydrogen interactions and geminal silanols where two OH groups are located on one silicon site. Several extensive studies were conducted using NMR\textsuperscript{4,7} and FTIR\textsuperscript{9-12} techniques for complete mapping of the surface of highly dispersible (HD) silica.

A similar structure of amorphous silica is expected to be obtained with the sol-gel process, where by means of hydrolysis of alkoxy silanes and subsequent condensation in the presence of catalyst, silica particles can be obtained.\textsuperscript{13,14} During the hydrolysis reaction the alkoxy silane is not always fully hydrolyzed into a silicic acid but some alkoxy groups may remain un-hydrolyzed. These groups can be trapped during the sol-gel reaction in the silica structure or on the surface. The possible presence of alkoxy groups in the \textit{in-situ} silica was briefly reported earlier\textsuperscript{15,16} indicating, for the first time, a possible different chemical structure of the silica obtained via the sol-gel reaction. The sol-gel reaction can be used as an alternative technique for silica formation in rubber materials for the purpose of reinforcing. Improved reinforcement by incorporation of fillers is reflected in the improvement of the mechanical properties (tensile strength, abrasion resistance, tear resistance and static and dynamic moduli). The reinforcement is commonly expressed via the Payne effect which is assumed to be related to the breakdown of
the filler-filler network in the rubber nanocomposite, observed as a drop in the modulus (the elastic modulus \(G'\) or the complex modulus \(G^*\)) with increase in strain. The difference between the modulus at low strain and the modulus at high strain is often used as a measure of the Payne effect. By comparing different types of filler it was found that the Payne effect is directly related to several properties of the filler, such as surface area, amount of filler, dispersion and surface chemistry of the filler.\(^{17-25}\)

The \textit{in-situ} nanocomposites reinforced with silica formed via the sol-gel reaction, showed better mechanical properties as compared to the conventional nanocomposites.\(^{26-28}\) The \textit{in-situ} nanocomposites consist of uniformly distributed single silica particles for which no particle-particle network formation is observed. Thus, the commonly accepted belief that the Payne effect originates only from the filler-filler network breakdown can be doubted, particularly since the effect was observed for rubber nanocomposites with low amount of filler (~ 5 wt%),\(^{29}\) supported with additional electrical conductivity measurements done by Funt,\(^{30}\) showing that the Payne effect may even exist in the absence of a filler-filler network. This was accompanied by a study from Sternstein and Zhu\(^{31,32}\) who claimed that the origin of the Payne effect is not only in the filler structure formation-destruction but also in the nature of the matrix. Based on this the authors proposed the so-called theory of trapped entanglements. The trapped entanglements are formed as a result of temporary bonding of rubber chains to the filler surface. These entanglements are not only expected to impede the mobility of the polymer segments in direct contact with the silica surface but also the mobility of other polymer chains leading to a change in the overall entanglement density of the matrix.

The improved rubber-silica interactions strongly depending from the polarity of the rubber (discussed in chapter 2) most probably will allow more intensive anchoring of rubber chains on the silica surface resulting in a larger number of trapped entanglements and consequently a greater effect on the overall entanglement density of the matrix.\(^{33}\) The rubber-silica interactions were considered
to be the key parameter for the improved reinforcement in rubber nanocomposites that triggered an extensive number of studies\textsuperscript{34-36} emphasizing their importance in the mechanisms responsible for the rubber reinforcement.

The improved mechanical properties of the \textit{in-situ} nanocomposites when compared to the conventional were ascribed to the uniform particle dispersion, existence of single particles instead of aggregates and the possible stronger rubber-silica interactions. The stronger rubber-silica interactions expected in the \textit{in-situ} nanocomposites were assigned to possibly less silanol groups present on the silica surface, resulting in lower hydrophilicity of the silica. Up to now, several studies\textsuperscript{37-39} have suggested, but never proved that there might be indeed less silanol groups on the \textit{in-situ} silica surface responsible for the improved rubber-silica interactions in the \textit{in-situ} nanocomposites. Usually the bound rubber\textsuperscript{40} is used as an indirect tool to estimate the intensity of these rubber-silica interactions, because it is directly related to the surface chemistry of the filler. The importance of the silica surface can also be seen in the various modification techniques\textsuperscript{41,42} for converting the silica surface into more hydrophobic and in that way improving the rubber-silica interactions and the compatibility with the rubber matrix.

Another disadvantage the rubber/silica conventional nanocomposites are facing in the current rubber industry is the ethanol produced during the silanization reactions. Removal of ethanol is very difficult because it has tendency to hydrogen bond with the silanol groups on the silica surface.\textsuperscript{43} Particularly for the \textit{in-situ} silica this might represent a problem because large amounts of ethanol are produced during the sol-gel reaction. For that reason in this chapter an effort will be made to detect the possible presence of ethanol. Moreover, there is a serious lack of information regarding the chemical structure of the obtained silica via the sol-gel reaction and consequently little or no understanding of the rubber-silica interactions, and therefore of the nature of the interface between the silica particle and the rubber matrix. Therefore, the focus in this chapter will be on a detailed chemical mapping of the silica made via sol-gel reaction in rubber matrix and its effect on the dynamic mechanical properties of the \textit{in-situ} silica nanocomposites.
4.2. Experimental section

4.2.1. Materials

The silica precursor, TEOS and the (n-hexylamine) catalyst were purchased from Aldrich and used as received. The characteristics of the two rubbers, namely natural rubber (NR; Tun Abdul Razak Research Centre), and ethylene-propylene-diene rubber (EPDM; Lanxess), are shown in Table 4.1. The type of silica used for conventional mixing is Zeosil 1165 MP produced by Rhodia, known as a highly dispersible (HD) silica commonly used in the rubber industry for the production of ‘green’ tires. It has a BET surface area of 150 m$^2$/g and an average particle size of 10 - 20 nm.

Table 4.1 Characteristics of rubber materials used.

<table>
<thead>
<tr>
<th>Rubber type</th>
<th>NR SMR L</th>
<th>EPDM Keltan 512</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Isoprene (1,4-cis)</td>
<td>Ethylene/Propylene/ENB 55/41/4.3</td>
</tr>
<tr>
<td>Impurity [wt%]</td>
<td>0.5</td>
<td>/</td>
</tr>
<tr>
<td>$M_w$ [kg/mol]</td>
<td>~800</td>
<td>260</td>
</tr>
<tr>
<td>Mooney viscosity</td>
<td>50-60 (100°C)</td>
<td>46 (125°C)</td>
</tr>
<tr>
<td>ML (1+4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_g$ [°C]</td>
<td>-65</td>
<td>-54</td>
</tr>
</tbody>
</table>

It was difficult to determine the exact molecular weight of the NR using gel permeation chromatography (GPC), because there was always residual gel. Literature $^{44}$ suggests an approximate $M_w$ value of 8x10$^5$ g/mol and $M_w/M_n = 2.3$.

Preparation of conventional EPDM nanocomposite (~10 wt% silica)

The conventional nanocomposites were prepared in an internal mixer ($V = 390$ cm$^3$) with tangential rotors and a fill factor of ~ 70 vol%. The starting temperature was 50 °C and the rotor speed was adjusted to reach temperatures above 140 °C. Usually for 10 wt% silica, a rotor speed of 110 rpm was enough to achieve the desired temperature (140 - 170 °C). The actual temperature of mixing
was kept at 140 - 160 °C, regardless whether a coupling agent was used or not, in order to maintain equal processing conditions for all samples. In the presence of TESPT coupling agent the temperature must be above 140 °C to start the silanization reaction but below 170 °C to prevent crosslinking of the rubber due to sulphur release from the coupling agent.

The mixing was performed in two steps. In the first step ZnO, stearic acid, half the amount of silica and half the amount of TESPT (if used) were added to the rubber and in the second step the remaining components were added. The mixing time of all components in the internal mixer was approximately 6 min. At the end, the so called ‘dump’ temperature of the mixture was measured. The dump temperature should be always above or equal to 140 °C to ensure that the silanization reaction is completed. The compound formulations used are shown in Table 4.2.

Table 4.2. Mixing parameters for EPDM conventional nanocomposites.

<table>
<thead>
<tr>
<th>Components [phr]</th>
<th>15 phr (10 wt%)*</th>
<th>15 phr (11 wt%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM/Keltan 512</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Silica/ZEOSIL 1165 MP</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Oil/Sunpair 2280</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Silane/TESPT</td>
<td>0</td>
<td>1.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>131</strong></td>
<td><strong>132.2</strong></td>
</tr>
</tbody>
</table>

*C Coupling agent (TESPT)

* Silica content of conventional nanocomposites as determined by TGA

It should be noted, that the silica content as measured by TGA was lower than when calculated from Table 4.2. In the rubber world the unit phr (parts per hundred rubber) is a commonly used measure because it simplifies the preparation of the formulations for the production of the conventional rubber/silica nanocomposites. In this text we will always refer to wt% of silica instead of phr. It should be noted that the content of inorganics (silica and ZnO) in the conventional nanocomposites was determined by TGA (averaged over two measurements) and the silica content was obtained after subtraction of the ZnO. The amount of silane...
(TESPT) used was 8 wt% with respect the amount of silica added to the sample. Even though the rubber compounds were not intended for vulcanization, stearic acid and ZnO were additionally added in order to approximate the same preparation conditions for the nanocomposites on an industrial scale. The ZnO is used as activator and the stearic acid as plasticizer and co-activator in the curing reaction (when performed).

**Preparation of in-situ (EPDM and NR) nanocomposites**

The target was to prepare NR and EPDM in-situ nanocomposites with fixed amount of silica of ~ 1 and ~ 10 wt% (see Table 4.3). The in-situ nanocomposites were prepared as described by Ikeda et al.\(^5\) Compression moulded rubber sheets with dimensions of 10 x 10 x 1.5 mm\(^3\) were swollen in TEOS and then immersed in a hexylamine solution at 80 °C. The in-situ nanocomposites were dried for 72 h at 50 °C under vacuum. A catalyst concentration in water of 0.096 mol/l and a constant weight ratio of H\(_2\)O:TEOS (5:1) was used.\(^5\)

**Table 4.3. Preparation of in-situ NR and EPDM nanocomposites with 1 and 10 wt% silica at 80 °C.**

<table>
<thead>
<tr>
<th>Silica [wt%]</th>
<th>TEOS amount [wt%]</th>
<th>Reaction time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Silica [wt%]</th>
<th>TEOS amount [wt%]</th>
<th>Reaction time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>33</td>
<td>600</td>
</tr>
</tbody>
</table>

It should be noted, that maximum swelling of EPDM rubber in TEOS at 80 °C was 33 wt%.

**Preparation of in-situ silica powder**

*In-situ* silica powder was prepared in the absence of rubber using 50 ml of TEOS mixed with 250 ml of an aqueous solution of hexylamine (0.096 mol/l), corresponding to 5:1 weight ratio of H\(_2\)O:TEOS. The sol-gel reaction proceeded
under intense stirring for 2 h at 40 °C until a milky mixture was obtained. The mixture was allowed to evaporate overnight in the fume-hood and then dried in an oven for 72 h at 50 °C under vacuum. The dried silica powder was additionally heated for 48 h at 110 °C under vacuum and a nitrogen flow in order to remove any remnant solvent. The HD silica was also dried for 48 h at 110 °C under vacuum and a nitrogen flow.

**Bound rubber determination**

**In-situ** and conventional rubber/silica nanocomposites with various silica amounts were immersed in THF, which is good solvent for the three rubbers. The ratio between the rubber/silica nanocomposites and the solvent was kept constant (2 % w/v) and the samples were immersed in the solvent for 48 h at room temperature while shaking. The residues were dried for 72 h at 50 °C under vacuum. The bound rubber content was calculated as following:

\[
Wt\% \text{ Bound rubber content} = \frac{w_{\text{residue}} - w_{\text{silica}}}{w_{\text{original}} - w_{\text{silica}}} \times 100
\]  

(4.1)

where, \( w_{\text{residue}} \) is the weight of the sample after solvent treatment in (g), \( w_{\text{original}} \) is the weight of sample before solvent treatment in (g) and \( w_{\text{silica}} \) is the weight of silica in (g) in the nanocomposite.

### 4.2.2. Characterization

**Thermogravimetric analysis - Infrared spectroscopy - Mass spectroscopy (TGA-FTIR-MS)**

The TGA-FTIR-MS measurements were performed in collaboration with Prof. Dr. Olivier Persenarie at the MateriaNova Institute in Mons, Belgium. The purpose of the measurements was to determine the organic components released from the in-situ silica at a particular temperature. The thermo-gravimetric analyses were performed on a TGA Q5000 from TA Instruments using nitrogen as purge gas. The analysis of the gases evolved during the thermal degradation was carried
out with a Bruker Tensor 27 FTIR spectrometer. Spectra were recorded (4000 to 600 cm\(^{-1}\)) owing to a gas cell heated at 225 °C and a mercury cadmium telluride (MCT) detector. The MCT detector is a photon (or quantum) detector that depends on the quantum nature of radiation and also exhibits very fast response. The MCT detectors must be maintained at liquid nitrogen temperature to be effective. In general, the MCT detector is faster and more sensitive than the deuterated triglycinesulfate (DTGS) detector. The evolved gases were also analyzed by mass spectrometry on a Thermostar quadrupolar apparatus from Balzers Instruments covering a mass range from 0 to 300 amu. Evolved gases were ionized by electron impact (70 eV). The simultaneous analysis of evolved gases by FTIR and MS spectrometers were made possible by a double coupling device. It consists of a Teflon-coated stainless steel « T » connexion which was heated at 225 °C thus avoiding any condensation of evolved gases. To this connexion the mass spectrometer is connected via a one-meter long quartz capillary (inner diameter = 150 µm) heated at 200 °C, and the gas cell of the FTIR spectrometer is connected through a one-meter long stainless steel tube (inner diameter: 2 mm) heated at 225 °C (N\(_2\) flow of 25 ml/min, heating rate 20 °/min).

**X-ray photoelectron spectroscopy (XPS)**

The XPS technique is a surface analysis method that provides information for the chemical composition of the material surface based on the obtained binding energies (eV). The measurements are carried out with a Thermo Scientific K-Alpha, equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained using an aluminium anode (Al K\(_\alpha\) = 1486.6 eV) operating at 72 W and a spot size of 400 µm. Survey scans were measured at a constant pass energy of 200 eV. The background pressure was 2 x 10\(^{-9}\) mbar and during measurement 4 x 10\(^{-7}\) mbar of Argon was used for the charge compensation as dual beam source. Dual beam source means that electrons and ions are present in the beam and since electrons are leaving there is charging of the sample. These low energy ions (no
sample damage) should compensate for the charging, because otherwise we might expect a shift in the values of the obtained binding energies and incorrect assignment of the appearing peaks.

**Magic angle spinning (MAS) Solid-state NMR**

The purpose of this technique was to provide in-depth knowledge for the chemical structure of the *in-situ* silica. The NMR measurements were performed in collaboration with Dr. M. R. Hansen and Cornelius Friedrich at the Max Planck Institute for Polymer Research in Mainz, Germany. The single-pulse $^1$H magic-angle spinning (MAS) NMR spectra were recorded on a commercial Bruker Avance I spectrometer with a Larmor frequency of 700.25 MHz for $^1$H using 25.0 kHz MAS in a 2.5 mm probe. 2D $^1$H-$^1$H double quantum-single quantum (DQ-SQ) correlation spectra were performed on a Bruker Avance III with a $^1$H resonance frequency of 850.27 MHz using a 2.5 mm probe and 25 kHz MAS spinning. For dipolar recoupling, excitation and reconversion of DQ coherences, we have used the Back-to-Back (BaBa) pulse sequence with a recoupling and reconversion time of 2 rotor periods, i.e. 80 µs. Both single-pulse $^{29}$Si and $^{29}$Si{$^1$H} cross-polarization/magic-angle spinning (CP/MAS) experiments were carried out on a Bruker Avance I spectrometer operating at a Larmor frequency of 700.25 MHz and 139.12 MHz for $^1$H and for $^{29}$Si, respectively, using a 4.0 mm probe. A MAS frequency of 10.0 kHz and proton decoupling (TPPM) were used to remove anisotropic interactions. In all experiments an r.f. frequency of 50.0 kHz was used corresponding to a 5.0 µs 90 degree pulse. For the single-pulse $^{29}$Si MAS NMR spectra a relaxation delay of 10 s was used, while for the $^{29}$Si{$^1$H} CP/MAS measurements we used a delay of 1.5 s. The CP contact time was set to 4.0 ms. In the $^{29}$Si{$^1$H} heteronuclear correlation experiments (HETCOR) the indirect dimension was sampled in 128 steps using a dwell time of 30.0 µs. The $^{13}$C{$^1$H} HETCOR spectrum was recorded on the same NMR spectrometer with a resonance frequency of 176.08 MHz for $^{13}$C in a 4.0 mm probe. A MAS frequency of 5.0 kHz and $^1$H TPPM decoupling during acquisition were applied. A relaxation delay of 3 s was used and the indirect dimension had 64 steps for a dwell time of 50.0 µs. The
CP contact time was set to 3.0 ms. The $^{15}$N$^{1}$H CP/MAS experiment was performed on a Bruker Avance II operating at a $^{15}$N Larmor frequency of 30.43 MHz and 300.23 MHz for $^1$H. A relaxation time of 3 s, 5.0 kHz MAS, $^1$H TPPM decoupling, and a CP contact time of 5.0 ms were used. The $^{13}$C$^1$H WISE NMR experiment was also carried out on that spectrometer with a Larmor frequency of 75.49 MHz for $^{13}$C. The spectrum was recorded at 4.0 kHz MAS using a 7.0 mm probe with a CP contact time of 3 ms. To prevent spinning sidebands in the $^{13}$C dimension the TOSS technique (total suppression of spinning sidebands) was applied.

**Infrared spectroscopy (FT-IR)**

Infrared spectra were recorded on conventional and *in-situ* silica powder samples using an Infrared EX Calibur spectrometer equipped with a Ge/KBr beam-splitter and a wide-band DTGS detector, in reflection mode at room temperature. The spectra were recorded in the range of 4500 - 650 cm$^{-1}$ and 100 scans were co-added for each measurement to have sufficient signal-to-noise ratio.

**Rubber process analyzer (RPA)**

The RPA is a specially designed rheometer for studying the dynamic mechanical properties of rubber materials. It contains a grooved die that prevents slippage of the material during the measurements at high strains (> 100 %). It generally measures the torque in the testing sample caused by the applied deformation. By applying a Fourier transformation the torque is divided into an elastic and viscous component that characterizes the dynamic mechanical properties of the material. Measurements were performed using RPA 2000 tester from Alpha technologies at 100 °C and a frequency of 0.50 Hz. The strain sweep was performed in the range of 0.56 to 1250 % strain.

**Transmission Electron Microscopy (TEM)**

The morphology of the nanocomposites was studied using the TEM. Ultrathin sections (70 - 100 nm) were obtained using a Reichert-Jung Ultracut E microtome equipped with a diatome diamond knife for dry cutting for trimming (45° angle)
and sectioning (35° angle) at temperature of -140 °C. The sections were placed on
200 mesh copper grid with a carbon supportive layer. The sections were examined
with the TEM Sphera instrument, FEI Tecnai 20 (operating voltage of 200 kV). It
should be noted, that later in the text it will be referred to structure and not
morphology of the nanocomposites.

4.3. Results and Discussion

4.3.1. Chemical structure of in-situ silica particles with FTIR

The in-situ silica in powder form used for the measurement was prepared as
everalized in Section 4.2.1. Infrared spectroscopy is well-known technique that can
provide chemical mapping of the various structural units on the silica surface using
their corresponding vibration bands. Infrared spectra of the in-situ and HD silica
were recorded as shown in Figure 4.1.

![FTIR spectra of in-situ and HD silica](image)

**Figure 4.1.** (a) FTIR spectra of in-situ and HD silica, (b) table with assignments of 1-5 peaks.

The FTIR spectra of in-situ and HD silica in Figure 4.1 show several characteristic
peaks, indicated as 1 to 5 in Figure 4.1, (b). The vibrations of the asymmetric
stretching of the Si-O-Si bonds are mainly in the range of 1000 - 1200 cm⁻¹. The
very intense broad band, appearing at 1063 cm⁻¹ for the in-situ silica and 1084 cm⁻¹
for the HD silica (peak 1) is assigned to a vibration perpendicular to the Si-O-Si bond while the weak shoulder appearing around 1200 cm\(^{-1}\) (peak 4) is assigned to a vibration parallel to the Si-O-Si bond.\(^{45, 46}\) The symmetric stretching vibration of Si-O-Si appears at 800 cm\(^{-1}\) (peak 3) and the Si-O in-plane stretching vibration from the silanol (Si-OH) groups appears at 950 cm\(^{-1}\) for the HD silica and at 962 cm\(^{-1}\) for the in-situ (peak 2).\(^{47}\)

The Si-O-Si network has another particular vibration in its bending mode appearing in the range of 465 - 469 cm\(^{-1}\) which in our case was not observed due to the limiting wavelength range of the FTIR instrument (650 cm\(^{-1}\)).\(^{48}\) It should be noted that the same vibration bands for both silica’s exhibit slightly different values. This might originate from the unequal concentrations of the corresponding chemical groups in both silica materials. Of our particular interest is peak 2, assigned to the Si-OH groups. This peak for the in-situ silica resembles more a low intensity shoulder than a well resolved peak when compared to the HD silica, indicating a possible lower presence of silanol groups on the in-situ silica surface. Unfortunately, from the spectra in Figure 4.1, (a) it was difficult to distinguish the individual presence of each type of silanol group, isolated, geminal and vicinal assigned to the following vibrations 3749 cm\(^{-1}\), 3736 cm\(^{-1}\) and 3745 cm\(^{-1}\), respectively.\(^2\) Another indication for possible less silanol groups present on the in-situ silica could be the intensity of water peak (peak 5), appearing in the range of 3300 - 3500 cm\(^{-1}\) and assigned to the O-H stretching. For the in-situ silica, the water band seems too weak and broad to be clearly observed, while for the HD silica it shows a somewhat higher intensity indicating a possibly higher water content. This might indeed suggest a more hydrophobic nature of the in-situ silica as compared to the conventional.

It can be expected the FTIR spectra of in-situ silica to reveal also the presence of ethoxy groups, due to the incomplete hydrolysis of the alkoxide precursor (TEOS), remnant TEOS and ethanol that is released as by-product during the sol-gel reaction. The ethanol can be either trapped inside the silica structure or be hydrogen bonded to the silanol groups on the surface.\(^{49, 1}\) The characteristic peak
assignments for these components are shown in Table 4.4.

Table 4.4. Assignments of TEOS, ethanol and silica$^{50-53}$

<table>
<thead>
<tr>
<th>TEOS [cm$^{-1}$]</th>
<th>Assignments</th>
<th>EtOH [cm$^{-1}$]</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1102</td>
<td>Si-O $\nu_{as}$</td>
<td>882</td>
<td>(C-C+C-O) $\nu_{s}$</td>
</tr>
<tr>
<td>1168</td>
<td>CH$_3$ rock</td>
<td>1050</td>
<td>C-C-O $\nu_{s}$</td>
</tr>
<tr>
<td>1299</td>
<td>CH$_2$ twist</td>
<td>1089</td>
<td>(C-C+ C-O)$\nu_{as}$</td>
</tr>
<tr>
<td>1400</td>
<td>CH$_2$ wag</td>
<td>1274</td>
<td>C-C-O $\nu_{as}$</td>
</tr>
<tr>
<td>1086</td>
<td>C-O $\nu_{as}$</td>
<td>1457</td>
<td>HCH $\nu_{as}$ bend</td>
</tr>
<tr>
<td>960</td>
<td>CH$_3$ rock</td>
<td>2975</td>
<td>CH$<em>3$ $\nu</em>{as}$</td>
</tr>
</tbody>
</table>

As can be seen in Figure 4.1, since some of the ethanol (1050 and 1089 cm$^{-1}$) and TEOS (1102 and 1168 cm$^{-1}$) peaks appear in the same region as the Si-O-Si vibrations, conclusions based solely on the FTIR results cannot be made. For the inverse emulsion the surfactant usually remains on the particle surface and is removed by calcination.$^{54}$ In analogy, assuming in-situ silica is formed via inverse micelles in the rubber matrix, as suggested by Ikeda et al.$^{55}$ one may expect to observe in the FTIR spectra of the in-situ silica also hexylamine with the characteristic vibration of the C-N bond (1000 - 1250 cm$^{-1}$).$^{56}$ However, no trace of a C-N bond was found in the recorded spectra.

4.3.2. Solid state NMR for silica structure determination

From physical and chemical perspective the structure of the in-situ silica is very important because it is indicative for the successfulness of the sol-gel reaction (full hydrolysis of the TEOS with no remnant ethoxy groups) and it significantly influences future applications of this material. For that reason detailed analysis of the chemical structure of in-situ silica was performed by Solid-state NMR using HD silica as reference material. A D$_2$O treatment is applied on the in-situ and HD silica in order to be able to distinguish between the silanol groups and the water present on the surface or/and inside the silica particles. This can be indicative for the possible higher hydrophobicity of the in-situ silica, as shown in Figure 4.2. The powder silica used in the measurements is prepared as elaborated in Section 4.2.1.
Chapter 4

Figure 4.2. Single-pulse $^1$H MAS NMR spectra of (a) HD silica and (b) in-situ silica dried at 120 °C under vacuum. Red lines show spectra of similar compounds after exchange with D$_2$O.

In Figure 4.2 (a) and (b), single-pulse $^1$H MAS NMR spectra of HD silica and in-situ silica (black lines), respectively are compared to their deuterated analogs (red lines). Exchange of protons with deuterons was obtained by stirring the pure compounds in D$_2$O overnight followed by drying under vacuum at 120 °C. Figure 4.2, (a) clearly shows that the OH groups at the HD silica surface can be exchanged by deuterons as indicated with the lower intensity of the D$_2$O exchanged peak (red line), whereas bulk-OH (hydrogen bonded silanol groups) as well as both germinal (OH)$_2$ and isolated OH species, do not show any effect which is consisted with their presence inside the silica. The bulk-OH and the water signals do not occur as sharp single resonances, but are spread out over a chemical shift range of up to 6 ppm (see Figure 4.2 (a)) and the isolated OH groups at the silica surface appear at a chemical shift range between 1.8 and 2.0 ppm.$^{57}$ An additional signal at 1.1 ppm was assigned to trapped isolated OH groups inside the silica particles.$^{58,59}$

For the in-situ silica shown in Figure 4.2, (b) the isolated OH (on the surface and trapped inside) and (OH)$_2$ groups were not observed, possibly due to the strong hexylamine resonances dominating the spectrum in that particular region. The signals assigned to hexylamine show a significant intensity decrease after the D$_2$O treatment indicating that the hexylamine molecules are adsorbed on the silica surface and probably due to the treatment, some are removed or washed away by
D$_2$O. The most interesting feature between *in-situ* and HD silica is the difference in the water peak. The presence of possibly less OH groups (more hydrophobic surface) on the *in-situ* silica can cause lower presence of physically bounded water on the surface, hence lower intensity of the water peak as observed in Figure 4.2 (b). In order to understand better this behaviour of the *in-situ* silica, further chemical mapping of the *in-situ* silica was provided by performing 2D $^{29}$Si $^1$H HETCOR NMR in comparison to HD silica, as shown in Figure 4.3.

Figure 4.3. 2D $^{29}$Si$^1$H HETCOR NMR spectra of (a) *in-situ* silica and (b) HD silica (c) schematic drawing of the possible silicon tetrahedra $Q^n$, with $n = 2, 3, 4$, corresponding to the number of siloxane bonds.

Figure 4.3 (a), shows the $^{29}$Si $^1$H HETCOR spectrum for the *in-situ* silica as compared to the HD silica. The spectrum reveals strong correlation between the $Q^3$ and the OH groups in the *in-situ* silica, as also observed for the HD silica in Figure 4.3 (b), showing evidence for the existence of OH groups on the silica.
surface. Interestingly, the remaining features observed for the in-situ silica in the NMR spectra are very different when compared to the ones observed for the HD silica. In the Figure 4.3 (a), the N-CH$_2$ (hexylamine) appears at 2.5 ppm and the CH$_3$ (methyl) group at 0.8 ppm. The ethoxy groups show correlations to both Q$^3$ and Q$^4$, indicating their presence not only on the surface (predominant presence of Q$^3$) but also inside the silica particles (predominant presence of Q$^4$). The correlation between the N-CH$_2$ group of the hexylamine and the Q$^3$ sites suggests that this polar group is possibly only located on the surface of the particles. Also, the strong bulk-OH or hydrogen bonded OH groups observed with the broad peak (3 - 8 ppm) in the HD silica are not observed for the in-situ silica. The reason can be that ethoxy groups and hexylamine on the silica surface might shield the OH groups from each other preventing them from forming hydrogen bonds.

In addition, to confirm the presence of hexylamine and ethoxy groups $^{13}$C {$^{1}$H} HETCOR was performed, as shown in Figure 4.4 (a). This spectrum primarily shows the intra-molecular correlations of hexylamine (numbers 1 - 6) with its directly bonded alkyl protons. Correlation peaks originating from ethoxy groups are very weak (A and B), reflecting the low abundance of these groups. The presence of hexylamine in both in-situ silica and the in-situ NR nanocomposites is verified by the $^{15}$N {$^{1}$H} CP/MAS NMR spectra, showing a single $^{15}$N resonance at - 347 ppm (Figure 4.4 (b) and (c)). For both of these samples $^{15}$N-labelled hexylamine was used during the synthesis. The reason for the use of $^{15}$N is the very low abundance of the nitrogen (0.37 %) thus low sensitivity during NMR measurement. The use of labelled $^{15}$N enabled detection of the hexylamine on the silica surface in the silica powder and the in-situ NR nanocomposite. This showed that indeed, in one step, a synthesis and modification on the in-situ silica was performed with no use of additional chemical compounds.
Another evidence for the presence of hexylamine only on the silica surface is provided via a measurement that gives an estimation for the mobility, as shown with the $^{13}\text{C}[^1\text{H}]$ WISE NMR spectrum in Figure 4.5.

It is estimated that the hexylamine dynamics observed for the in-situ silica belongs to an intermediate regime (~ 20 - 50 kHz) indicating a mobility which is somewhere between rigid and mobile. A rigid hexylamine (trapped inside the silica structure) would appear as a broad signal with a spectral width of up to 100 kHz, while mobile hexylamine (free non-bounded) would give rise to a sharp and narrow lines. Based on these results it seems that hexylamine molecules are trapped inside
the silica particles. It is likely that the hexylamine molecules are attached to the silica surface in neither a fully rigid nor a fully mobile state, but in an intermediate state. In addition, the quality of the in-situ and the HD silica is determined with the ratio of $Q^4 : Q^3 : Q^2$ as shown in Figure 4.6.

![Figure 4.6](image)

**Figure 4.6.** Quantitative single-pulse $^{29}$Si MAS NMR spectra of (a) HD silica, (b) in-situ silica, and (c) the in-situ NR nanocomposite.

Figure 4.6 shows the quantitative single-pulse $^{29}$Si MAS NMR spectra of (a) HD silica, (b) in-situ silica, and (c) the in-situ silica in the in-situ NR nanocomposite. In general, three different peaks are observed: at -91.7 ppm, at -101.4 ppm, and at -110.9 ppm, corresponding to $Q^2$, $Q^3$, and $Q^4$ silicon tetrahedra, respectively.\(^5,6\)

As shown in Figure 4.3 (d), $Q^2$ might correspond to a silicon atom carrying two hydroxyl groups, two ethoxy groups, or one of each group, $Q^3$ is connected to either one hydroxyl or one ethoxy group, and $Q^4$ has only siloxane bonds.

While with the FTIR analysis it was difficult to distinguish between the different silanol groups existing in the in-situ silica, here there is an evidence for their existence in a possibly somewhat modified form. The quality of the in-situ silica (1.4:23.9:74.7) when compared to the HD silica (1.4:23.2:75.4) is very similar, while slightly different quality (1.8:30.0:68.2) is obtained for the silica in the in-situ NR nanocomposite. The results show that the quality of the silica made via sol-gel reaction is almost the same as the one of the HD silica. The reason for the lower quality of the in-situ silica inside the rubber matrix can be ascribed to the diffusion limitations of the reactants inside the rubber matrix resulting in lower degree of condensation.
Interestingly, the ratio between \( Q^2 \) and \( Q^3 \) for \textit{in-situ} and HD silica is very similar. The only difference is that the \textit{in-situ} silica contains not only Si-OH but also ethoxy (Si-OCH\(_2\)CH\(_3\)), which indicates less presence of OH groups on the \textit{in-situ} silica as compared to the HD silica. This finally resolves a piece of the puzzle for the chemical structure of the \textit{in-situ} silica where indeed it may be said that not only it contains less Si-OH groups, but also residual ethoxy groups from the TEOS and hexylamine that contributes additionally to its hydrophobic nature.

The NMR study provided indeed a more detailed analysis of the chemical structure of the \textit{in-situ} silica detecting the presence of ethoxy groups and hexylamine. Figure 4.4 in Section 4.3.2 suggests a good correlation between the N-CH\(_2\) and the \( Q^3 \) sites indicating close proximity (~4 angstroms) of the polar amino head of the hexylamine and the silanol groups on the silica surface. However, it cannot provide information for the type of interactions existing between these two chemical groups. For that purpose, X-ray photoelectron spectroscopy (XPS) was used to provide better insight into the type of interactions existing on the \textit{in-situ} silica surface.

\textbf{4.3.3. Mapping \textit{in-situ} silica surface by X-ray photoelectron spectroscopy (XPS)}

XPS is a spectroscopic technique used for mapping the elemental composition of a particular material. The sample is irradiated with X-rays that can travel until about 10 nm depth into the material and result in the ejection of electrons from the orbitals of the analysed sample. The parameters measured are the kinetic energy, used to obtain the binding energy of a particular bond, and the number of electrons released during the measurement, used for the calculation of the atomic concentrations. XPS was performed on \textit{in-situ} silica in powder form (as elaborated in Section 4.2.1) and HD silica. The chemical components detected are presented in Table 4.5.
Table 4.5. XPS assignments of in-situ and HD silica.

<table>
<thead>
<tr>
<th>Atomic orbitals</th>
<th>Type of bond</th>
<th>Binding energy [eV]</th>
<th>Atomic conc. [%]</th>
<th>In-situ silica</th>
<th>HD silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>C-C/C-H</td>
<td>284.4161</td>
<td>5.36</td>
<td>284.8</td>
<td>1.33</td>
</tr>
<tr>
<td>C1s</td>
<td>C-O</td>
<td>285.8187</td>
<td>1.42</td>
<td>286.2</td>
<td>0.5</td>
</tr>
<tr>
<td>C1s</td>
<td>C=O</td>
<td>287.3389</td>
<td>0.35</td>
<td>287.7</td>
<td>0.16</td>
</tr>
<tr>
<td>N1s</td>
<td>NH2-free</td>
<td>399.1666</td>
<td>0.42</td>
<td>405.2</td>
<td>/</td>
</tr>
<tr>
<td>N1s</td>
<td>NH2-H.B</td>
<td>401.4041</td>
<td>0.28</td>
<td>401.6</td>
<td>/</td>
</tr>
<tr>
<td>Na1</td>
<td>Na</td>
<td>1078.427</td>
<td>/</td>
<td>1072.7</td>
<td>0.37</td>
</tr>
<tr>
<td>O1s</td>
<td>O-(Si, H,C)</td>
<td>532.6263</td>
<td>64.4</td>
<td>532.6</td>
<td>68.5</td>
</tr>
<tr>
<td>Si2p</td>
<td>SiO</td>
<td>103.3001</td>
<td>27.8</td>
<td>103.3</td>
<td>29.1</td>
</tr>
</tbody>
</table>

The XPS data presented in Table 4.5 additionally confirm the difference in the surface chemistry between the in-situ and HD silica. The first difference originates from the total carbon content which for in-situ silica is ~ 7.15 % and for the HD is ~ 2 %. The higher carbon content for in-situ silica can be ascribed to the presence of remnant ethoxy groups, hexylamine and absorbed air. The carbon observed for the HD silica can be assigned only to the absorbed air (CO₂). This was proven by removing a layer (10 - 15 nm) from the surface of the HD silica with argon and performing the XPS measurement again, which showed no presence of carbon. Three types of carbon peaks are shown in Table 4.5 and assigned to C-C/C-H, C-O and C=O bonds appearing at 284.4 eV, 285, 8 eV and 287.3 eV binding energy, respectively. Particularly, the higher concentration of the C-O bond (1.42 %) for the in-situ silica additionally is consistent with the presence of ethoxy groups on the surface. The C-O bond can also originate from the ethanol which is a by-product of the sol-gel reaction and may be located on the silica surface. Unfortunately, with XPS we cannot make a clear distinction between the ethoxy groups and the ethanol. Moreover, the amino group of the hexylamine (NH₂) resulted in two characteristic peaks, at 401.4 eV, assigned to a hydrogen bonded amine, and at 399.16 eV. Earlier studies suggested two different origins of the peak appearing at 399.16 eV, thus to a free amine and to a chemisorbed amine. It is believed that the chemisorbed hexylamine bonds to the silica surface via formation of a Si-N bond. Since in our
case, even at 500 °C (see Figure 4.10 (a)) release of hexylamine is still observed, the presence of chemisorbed type of amine is more likely to be present than the free amine.

Moreover, since the in-situ silica is formed via a sol-gel reaction that proceeds via an ionic mechanism where the hexylamine, becomes protonated by accepting a proton from the water, it was expected to observe an ionic interactions between the positively charged hexylamine and remnant negatively charged silica intermediates on the in-situ silica surface. The ionic interactions should result in a peak at 402.8 eV \(^2\) which here was not observed. This shows that hexylamine is attached to the silica surface only via hydrogen bonding and chemisorption. The O(1s) binding energy for the in-situ and HD silica appears at 532.6 eV and corresponds to all components bonded to the oxygen such as O-Si, O-H and O-C, that in principal have very close binding energies and are difficult to distinguish. The Si (2P) binding energy is in the range of 103.3 eV corresponding to a Si-O-Si network.

Since NMR and XPS cannot distinguish well between the ethoxy groups present from the partially hydrolyzed alkoxy precursor (TEOS) and possible present ethanol molecules, additional information is obtained by utilizing three techniques at the same time. These techniques combine the advantages of the thermo-gravimetric analysis, infrared spectroscopy and mass spectroscopy (TGA-FTIR-MS) which allows real time detection of the chemical compounds released during the thermal treatment of the silica. The detection of ethanol is very important because it can accumulate around the particle surface and prevent good compatibility between the silica and the rubber matrix, which consequently can have a negative effect on the mechanical properties of the in-situ nanocomposites.

### 4.3.4. Time-resolved thermal treatment of in-situ silica with FTIR-TGA-MS

The physical and chemical changes of the HD silica during a thermal treatment are well reported in earlier studies while the information available for the in-situ silica is still very limited.\(^1\) The purpose of using a combinatory TGA-FTIR-MS is to be able to estimate whether ethanol is present in the silica
particle and to approximate the way it is bonded to the silica surface (physical or chemical interactions) by using the temperature at which it starts to evolve. It should be noted that precise determination of the exact temperature at which one compound begins to evolve is difficult because there is always certain delay between the evaporation of the compounds in the TGA instrument and their detection by the FTIR and the MS instrument. For that reason when assigning a temperature, at which certain compound evolves, one must consider narrow temperature region instead of one particular temperature. Spectra of the thermal treatment of \textit{in-situ} (as elaborated in Section 4.2.1) and HD silica with simultaneous use of TGA-FTIR-MS are presented in Figure 4.7.

![Figure 4.7. 3D time resolved spectra of a heat treatment of HD (a) and in-situ (b) silica as followed by combinatory TGA-FTIR-MS during heating until 1000 °C with a rate of 20 °C/min.](image)

Figure 4.7 shows the evolution of chemical compounds at particular temperature regions during heating of HD and \textit{in-situ} silica. On both spectra, mainly water peaks are observed in the range of 1300 - 1800 cm\(^{-1}\) and 3200 - 3800 cm\(^{-1}\) and the carbon dioxide (CO\(_2\)) peak at 2350 cm\(^{-1}\) indicated accordingly with the black dashed lines to guide the eye.\(^{56}\) The extensive carbon dioxide evolution is assigned to the intensive decomposition of organics evolving from the \textit{in-situ} silica at these high temperatures while in the HD silica possibly due to absorption of air, as already confirmed by XPS (Section 4.3.3). In addition, the FTIR spectrum of \textit{in-situ} silica in Figure 4.7, (b) also suggests the presence of other smaller peaks
appearing at different wavelengths, which can be ascribed to an evolution of other compounds besides water and CO$_2$. The magnitude of the chemical changes occurring in the *in-situ* and the HD silica during the thermal treatment is illustrated by the weight loss shown in the four temperature regions in Figure 4.8. The total weight loss for the *in-situ* silica as summarized from each region (15.3 %) is higher than for the HD silica (9.48 %), indicating a higher concentration of organic compounds present in this material.

![Figure 4.8. DTG thermograms of in-situ silica and conventional obtained during thermal treatment until 1000 °C.](image)

In *region 1* (25 - 150 °C) of Figure 4.8, weight losses were caused only by the removal of physical water from both materials. For the *in-situ* silica FTIR and MS confirmed that only water (no other organics) was removed in this interval. Even though the two silica materials were dried under the same conditions the *in-situ* silica shows presence of less adsorbed physical water (1 %) than the HD silica (2 %), indicating again a lower affinity towards water. This we might assign to the more hydrophobic nature of the *in-situ* silica due to the ethoxy groups and the hexylamine residing on the surface, as shown earlier in this chapter. In regions 2 (150 - 330 °C) and 3 (330 - 490 °C) more intensive chemical changes occur in the *in-situ* and HD silica resulting in release of chemically bonded water, rapid condensation of the silanol groups in both materials and for the *in-situ* silica additional release of organic components, as indicated by the FTIR spectra.
shown in Figure 4.9.

![Figure 4.9](image)

Figure 4.9. (a) FTIR spectra of in-situ silica at different temperatures and (b) comparison of HD and in-situ silica at approximately 330 °C.

In Figure 4.9, (a) the FTIR spectra of in-situ silica suggests presence of hexylamine (1121 cm\(^{-1}\)) and ethanol (1055 cm\(^{-1}\)) that begin to evolve at approximately 300 °C, indicating their presence on the silica surface via formation of hydrogen bonds. It was already shown from the XPS results (see Table 4.5) that hexylamine is hydrogen bonded and we expect ethanol to be also hydrogen bonded to the OH groups on the silica surface. The hexylamine and ethanol in the in-situ silica were assigned from the corresponding absorption bands of the pure components determined in their gas phase (FTIR-TGA), as shown in Table 4.6. Another peak that shows a similar trend with temperature as the other two peaks appears in the range of 1220 - 1225 cm\(^{-1}\) is difficult to assign because it does not correspond to any of the components mentioned in Table 4.6. However, this absorption peak is close to the one of ethanol (1242 cm\(^{-1}\)) and since MS does not suggest the presence of other relevant compounds, we might assume that it originates from the ethanol. The difference between the in-situ and HD silica for the same temperature conditions (~ 330 °C) is clearly observed in Figure 4.9 (b), where the HD silica does not show presence of organics, as indicated by the absence of any peaks in the particular region (600 - 1400 cm\(^{-1}\)).
Table 4.6. FTIR assignments of pure hexylamine, ethanol and TEOS in their gas phase determined with TGA-FTIR.

<table>
<thead>
<tr>
<th>Hexylamine [cm⁻¹]</th>
<th>Ethanol [cm⁻¹]</th>
<th>TEOS [cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1124</td>
<td>1055</td>
<td>1393</td>
</tr>
<tr>
<td>1408</td>
<td>1116</td>
<td></td>
</tr>
<tr>
<td>1242</td>
<td>961</td>
<td>793</td>
</tr>
</tbody>
</table>

It should be noted that presence of non-reacted TEOS in the \textit{in-situ} silica powder and the \textit{in-situ} nanocomposite was not observed, suggesting good conversion and/or proper drying conditions. Three possible sources can be distinguished for the organics (hexylamine and ethanol) released from the \textit{in-situ} silica: i) residuals from the sol-gel reaction strongly bounded on the silica surface, ii) trapped inside the silica particles and iii) released during a post-condensation reaction triggered by the extreme temperature conditions. Possible evidence for the post-condensation reaction is provided by the MS spectra recorded during the thermal treatment of the \textit{in-situ} silica as shown in Figure 4.10. The hexylamine, ethanol and water were followed by the ionization species with 30, 31 and 18 mass-to-charge ratios (m/z), respectively as a function of time and temperature. These particular ionized species are selected because in the MS spectra of their pure components (hexylamine, ethanol and water), give the highest abundance.
Figure 4.10, suggests relatively low presence of ethanol and hexylamine with intensities ranging between $10^{-11}$ - $10^{-10}$ when compared to the water that is significantly higher $10^{-8}$ - $10^{-7}$. There are several reasons for the higher amount of water, such as: condensation of silanol groups, strong hydrogen bonded water on the surface or in the small micropores in the silica surface and possibly trapped water molecules in the *in-situ* silica structure that can be released at high temperatures. Additionally, in this temperature region (region 4: 490 - 650 °C) maxima in the intensities for all three components (hexylamine, ethanol and water) are observed. These maxima possibly originate from the post-condensation reaction, during which an additional amount of ethanol and water is formed. However, we cannot also exclude the possibility that ethanol molecules might be also trapped inside the silica particles and become suddenly released in this temperature region.

It should be noted that the ethanol amount is surprisingly low. A possible reason can be the hydrophobic surface on the *in-situ* silica which limits the number of ethanol molecules that interact via hydrogen bonds with the Si-OH groups. In addition, the presence of residual ethoxy groups inside the silica particles also creates unfavourable environment for the ethanol to remain trapped during the sol-gel reaction. The temperature region of the observed maxima in Figure 4.10...
corresponds well to the extensive evolution of CO₂ in the same temperature range (see Figure 4.7, (b)), related to intensive decomposition of the high amount of organics released.

The conducted study suggests that in-situ silica formed via the sol-gel reaction has a chemical structure very different from the HD silica. The presence of the ethoxy groups has been confirmed inside and on the silica surface accompanied by the hexylamine molecules. This provides a unique chemical structure of so-called ‘hairy’ silica particles, schematically represented in Figure 4.11.

These ‘hairy’ silica particles are expected to develop a better compatibility with the rubber matrix and consequently improve the mechanical properties of the in-situ rubber/silica nanocomposites.

4.3.5. Payne effect and reinforcing mechanism of in-situ silica nanocomposites

4.3.5.1. Comparison of in-situ and conventional EPDM nanocomposite

In general, reinforcement is defined as the improvement in the mechanical properties by addition of fillers and is commonly expressed by the Payne effect.¹⁷,⁶⁴ Reinforcement is a complex phenomenon for which not one, but several
mechanisms can be considered responsible. For the in-situ nanocomposites three important parameters are known to be crucial for achieving excellent reinforcement, such as: small particle size (~30 - 50 nm), their uniform dispersion throughout the rubber matrix and the hydrophobic nature of these particles. In order to evaluate the effect of these parameters on the reinforcement at 10 wt% silica loading, RPA measurements were conducted on in-situ and conventional (with and without coupling agent) EPDM nanocomposites, as shown in Figure 4.12. The in-situ and the conventional nanocomposites are prepared as described earlier in this chapter.

Figure 4.12. Elastic moduli ($G'$) vs strain for (a) in-situ, (b) conventional nanocomposites and (c) conventional nanocomposites with coupling agent (CA) for silica loading of 10 wt%, (left) TEM images (scale 0.2 μm) representing the structure of the three nanocomposites, respectively.

Figure 4.12 shows the change of the dynamic elastic modulus with strain for the three nanocomposites. A higher modulus at low (2%) and high (200%) strain is obtained for the in-situ nanocomposite as compared to the conventional ones, even when prepared in presence of coupling agent, as shown in Figure 4.13.
Figure 4.13. (a) Elastic moduli \( (G') \) for in-situ and conventional (with coupling agent) nanocomposites at 2 and 200 % strain.

The modulus of the in-situ nanocomposite is 50 - 60 % higher as compared to the ones of the conventional nanocomposites (with and without coupling agent). In the case of the conventional nanocomposites, it is generally accepted that the high modulus at low strain are ascribed to several parameters such as: larger size of the silica aggregates (> 150 nm), their non-uniform dispersion and the strong degree of filler networking formed as a result of strong silica-silica interactions. By improving the rubber-silica interactions via chemical modification of the silica surface or use of coupling agents these parameters can be improved resulting in a lower modulus at low strain, thus a smaller Payne effect and better reinforcement, shown in Figure 4.12. The modulus at high strain is commonly related to the strength of the rubber-silica interactions resulting in a higher modulus for stronger interactions (see Figure 4.13).

Interestingly, the in-situ nanocomposite with excellent dispersion of small single particles and no filler-filler network formation (see Figure 4.12, (a)), instead of lower modulus, showed higher modulus as compared to the conventional nanocomposites. There are two possible reasons that can contribute to this interesting behaviour: the large number of small size (40 ± 5 nm) silica particles and their unique surface chemistry.

The small single particles provide a large surface area for interaction with the
rubber, acting as additional crosslink\textsuperscript{66} that influences the entanglement density of the entire rubber matrix causing stiffening. The more hydrophobic surface of the \textit{in-situ} silica plays an important role in the intensity of the rubber-silica interactions and the tendency of the rubber chains to anchor on the silica surface, forming the so-called trapped entanglements.

In the absence of a filler-filler network, the drop in the modulus (Payne effect) in the \textit{in-situ} nanocomposite can be ascribed to the disentanglement of these trapped entanglements that begin to slip and detach from the silica surface, resulting in overall softening of the rubber matrix.\textsuperscript{67,68} The process of disentanglement and slippage is expected to intensify with increase of strain until a strain of 1000 \% is reached. At this high strain all moduli end-up in one single point indicating that possibly most of the trapped entanglements are disentangled and only the effect of the matrix remains. An indirect estimation for the strength of the rubber-silica interactions can be obtained from the bound rubber content, where stronger interactions promote higher bound rubber content, as shown in Table 4.7.

\begin{table}[h]
\centering
\begin{tabular}{lcc}
\hline
Type of EPDM nanocomposite  & \multicolumn{2}{c}{Bound rubber [wt\%]} \\
(10 wt\% silica)         & In-situ          & Conventional No CA* \ \\
                          & 33              & 18.5 \ \\
                          & CA*             & 23              \\
\hline
\end{tabular}
\caption{Bound rubber of \textit{in-situ} EPDM nanocomposite as compared to EPDM conventional nanocomposites ($T_{room}$, THF).}
\end{table}

Table 4.7 shows a higher bound rubber obtained for the \textit{in-situ} nanocomposite (33 wt\%) as compared to the conventional nanocomposites, even when prepared with a coupling agent. This additionally supports the high moduli obtained at low and high strain for the \textit{in-situ} nanocomposite (see Figure 4.13).

In order to understand the reinforcement mechanisms acting in the \textit{in-situ} and the conventional nanocomposites, one must consider the essentially different morphologies existing in these two materials: uniformly dispersed single silica particles in the \textit{in-situ} nanocomposites and silica aggregates building a filler-filler network.
network in the conventional nanocomposites. Thus, the same principles for understanding the reinforcement mechanisms cannot be applied in both materials and two different approaches should be considered: the network approach for the conventional nanocomposites, where indeed the filler-filler network has a major effect and the filler-particle approach, where the particle size and nature of the rubber-silica interface plays a crucial role.

4.3.5.2. Effect of rubber type and silica loading on in-situ nanocomposites

It is expected the silica content and rubber type in the in-situ nanocomposites also to have an effect on the modulus. Therefore, the modulus of in-situ NR and EPDM nanocomposites at 1 and 10 wt% silica, are shown in Figure 4.14.

![Figure 4.14. Elastic moduli ($G'$) of in-situ NR and EPDM nanocomposites for silica loading of ~ 1 and 10 wt% as determined from the RPA measurements (TEM images are at 100 nm scale).](image)

Figure 4.14 shows an increase in the modulus at low and high strain in both nanocomposites with increase in silica content. The magnitude of this increase, varies in both materials. In-situ NR nanocomposite shows a higher modulus at low strain as compared to the modulus for the EPDM nanocomposite for the same silica content, as shown in Figure 4.15.
The higher silica loading of 10 wt% results in a significant improvement of the modulus for both materials with a somewhat higher modulus at low strains for the in-situ NR nanocomposite. The reason for the different moduli at low strain between the in-situ NR and EPDM nanocomposites can be due to the different morphology, as illustrated with the TEM images in Figure 4.14. The images suggest that for same silica content more particles with smaller size (23 ± 3 nm) are observed for the NR as compared to the EPDM (40 ± 5 nm) nanocomposite. This difference in particle size is expected to have a high impact on the overall entanglement density of the matrix resulting in higher stiffening. In addition, the higher amount of bound rubber obtained for the in-situ NR nanocomposite (see Table 4.8) is expected to additionally increase the modulus at low strain.

Table 4.8. Bound rubber content ($T_{room}$, THF, shaking) of NR and EPDM in-situ nanocomposites.

<table>
<thead>
<tr>
<th>Silica [wt%]</th>
<th>Bound rubber [wt%]</th>
<th>EPDM</th>
<th>NR</th>
</tr>
</thead>
<tbody>
<tr>
<td>~ 1</td>
<td>10</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>~ 10</td>
<td>33</td>
<td>66</td>
<td></td>
</tr>
</tbody>
</table>

As an additional indication for good rubber-silica interactions, the change in the glass transition temperature ($T_g$) between the pure rubber and the nanocomposite
Chapter 4

with different silica content is commonly used. It is expected $T_g$ to shift towards higher temperatures for stronger rubber-silica interactions as a result of the reduced mobility of the polymer chains around the silica particle.\textsuperscript{23} In our case, the change between the $T_g$ of the pure rubber and the nanocomposite was only ($\sim 2 - 3 \, ^\circ C$). This indicates that the high moduli at high strain are not only due to the stronger rubber-silica interactions but also due to other parameters (large surface area and change in the entanglement density of the matrix) that together have a cumulative effect strongly influencing the reinforcement in the \textit{in-situ} nanocomposites.

Another possible explanation for the improved mechanical response of the \textit{in-situ} nanocomposites is the possibility of having a rubber chain trapped inside the silica particle. This hypothesis was supported by the MAS-NMR measurements as shown in Figure 4.16.

Figure 4.16. $^{29}\text{Si} \, (^1\text{H})$ HETCOR spectra of (a) EPDM conventional and (b) \textit{in-situ} nanocomposite with $\sim 10$ wt% silica (c) schematic representation of a trapped chain inside \textit{in-situ} silica particle.

Figure 4.16 shows the $^{29}\text{Si} \, (^1\text{H})$ HETCOR spectrum of the \textit{in-situ} EPDM and the conventional nanocomposite. The most surprising feature in Figure 4.16 (a) is the large peak appearing at $\sim 0.8 \, \text{ppm}$ due to strong correlation between the CH$_3$ group
and \( Q^4 \) in the \textit{in-situ} EPDM nanocomposite.

The \( CH_3 \) group can be easily assigned to the ethoxy groups or the hexylamine, as we observed previously from the \(^{29}\text{Si} \) \((^1\text{H})\) HETCOR for the \textit{in-situ} silica (see Figure 4.3). In this case, a possible explanation for this rather unexpected behaviour is that the \( CH_3 \) group originates from the EPDM (the propylene unit) rubber itself and the only way to strongly correlate with \( Q^4 \), which is mainly present in the interior of the silica representing the Si-O-Si network, is by being trapped inside the silica particles (see Figure 4.16 (c)). The absence of the \( CH_3 \) peak in the EPDM conventional nanocomposite (Figure 4.16 (b)) additionally contributes to our hypothesis for a rubber chain trapped inside silica particle. The same correlation is also observed in the \textit{in-situ} NR nanocomposite, which means this may occur regardless of the rubber type.

It can certainly be expected that these trapped chains can additionally explain the good mechanical properties of the \textit{in-situ} nanocomposites.

\textbf{4.4. Conclusions}

The sol-gel gel reaction in rubber resulted in formation of naturally modified silica particles with hexylamine and ethoxy groups residing on the surface as was shown using several characterization techniques. It was shown that ethoxy groups are present inside the silica as well as on the silica surface, while hexylamine resides particularly on the surface contributing additionally to the hydrophobicity of the \textit{in-situ} silica. In addition, it has been shown that the composition of the \textit{in-situ} silica expressed with \( Q^2 \), \( Q^3 \) and \( Q^4 \) is very similar to the composition of the HD silica indicating good quality. Moreover, the excellent dispersion of the \textit{in-situ} silica particles and their hydrophobic surface, combined with a possibly trapped rubber chains provided good basis for achieving excellent mechanical properties. The interpretation of the Payne effect in the \textit{in-situ} nanocomposites showed to be somewhat different than commonly known for the conventional nanocomposites. This can be ascribed to the essentially different structure of these two materials, hence silica aggregates versus single-particle morphology in the conventional and \textit{in-situ} nanocomposites, respectively.
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Preparation of in-situ nanocomposites via sol-gel reaction in rubber matrix under dynamic conditions: one-step reactive extrusion

Abstract

The processing of the in-situ nanocomposites via batch mixer and reactive extrusion is addressed. The materials produced via batch mixing showed significantly higher silica contents for the same reaction time as compared to the in-situ nanocomposites prepared under static conditions. The structure of the obtained nanocomposites was significantly different, hence consisting not only of single silica particles but also aggregates and silica regions. In-situ nanocomposites were also successfully produced via reactive extrusion. The nanocomposites obtained in this way had a maximum loading of 3.2 wt% silica, possessed a uniform dispersion of silica particles (higher particle size polydispersity) and very good properties, even when compared to conventional nanocomposite with 10 wt% silica and a coupling agent (CA).
5.1. Introduction

The requirements for various properties of nanocomposite materials, composed usually from an organic matrix and inorganic filler, are imposed by their increasing application in a widely different areas as reinforcing materials, bio-inspired hybrid materials, protective and decorative coatings, micro-electronics and optics. In order to satisfy the application requirements the need for increased productivity is the biggest challenge which technology is facing at the moment. The most efficient way to continuously produce nanocomposites would be via melt processing, using one of the common techniques known to industry, namely extrusion and injection moulding. However, the reason these techniques are not well exploited so far is the difficult dispersion of the nano-sized particles in the polymer due to their very small size and strong tendency to agglomerate. These properties of the particles, in combination with the large difference in compatibility with the polymer matrix, result in very difficult mixing. Nevertheless, a small particle size and good dispersion throughout the matrix are essential for good reinforcement and mechanical properties.

There are several ways reported in literature regarding the possibilities to improve the compatibility between the polymer and the filler, such as: in-situ polymerization, filler surface modification and the use of so-called organic/inorganic concentrates.

The in-situ polymerization method involves dispersion of (modified) silica particles into a monomer solution followed by polymerization of the mixture. It is expected that the in-situ polymerization diminishes the agglomeration problem associated with traditional mixing via extrusion but still cannot meet the demands for industrial production. The goal of the surface modification is to modify the surface of the hydrophilic filler (e.g. silica) into a more hydrophobic surface by attaching different chemicals, usually with long hydrophobic tails. An example is the modification of silica with vinyl trimethoxysilane (VTMS) that was mixed with polyethylene (PE) via single screw extrusion. The use of the organic/inorganic concentrates of modified silica and polymethylmethacrylaat (PMMA) or
polystyrene (PS)\(^2\) is another way to improve the production of the nanocomposites via extrusion. The concentrate is actually the polymer loaded with a high silica content. These concentrates can be prepared prior to extrusion via solution blending and \textit{in-situ} polymerization. The concentrate is used in the extrusion as a starting material, instead of the pure particles, which significantly decreases the problem with particle agglomeration. In addition, the compatibility with the matrix is improved, so that the mixing results in better silica dispersion and increased productivity of the nanocomposites with higher silica content.\(^2\)

Another possibility that has great potential to become industrially applicable is the preparation of \textit{in-situ} nanocomposites via sol-gel reaction using a pre-hydrolyzed silica precursor, called hyperbranched polyalkoxysilane (PAOS), instead of pure alkoxysilane via reactive extrusion using water vapor instead of liquid water.\(^{14-16}\) So far, the sol-gel reaction was performed only on laboratory scale and appreciated for its mild reaction conditions under which it proceeds.\(^{17-19}\) However, this process almost always resulted in very long reaction times needed for the silica formation, which is unacceptable for industrial production where very short reaction times are required.

Therefore, the need for a method of producing \textit{in-situ} inorganic/organic nanocomposites via industrial processes still remains. For that purpose in this chapter, the transition from laboratory scale to dynamic production of \textit{in-situ} nanocomposites and reactive extrusion is shown. The target was to produce in one step \textit{in-situ} nanocomposites with certain silica loading and properties comparable to the conventional nanocomposites, while at the same time eliminating the problems associated with the extensive mixing and agglomeration of the silica particles.

5.2. \textit{Experimental section}

5.2.1. \textit{Materials}

The silica precursor, TEOS and the (n-hexylamine) catalyst were purchased from Aldrich and used as received. The characteristics of the three rubbers, namely
natural rubber (NR; Tun Abdul Razak Research Centre), styrene-butadiene rubber (SBR; Lanxess) and ethylene-propylene-diene rubber (EPDM; Lanxess), are shown in Table 5.1. The type of silica used for conventional mixing is Zeosil 1165 MP produced by Rhodia, known as a highly dispersible (HD) silica commonly used in the rubber industry for the production of ‘green’ tires. It has a BET surface area of 50 m$^2$/g and an average particle size of 10 - 20 nm.

*Table 5.1 Characteristics of rubber materials used.*

<table>
<thead>
<tr>
<th>Rubber type</th>
<th>NR SMR L</th>
<th>EPDM Keltan 512</th>
<th>SBR VSL 5025-0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition [wt%]</td>
<td>Isoprene (1,4-cis)</td>
<td>Ethylene/Propylene/ENB 55/41/4.3</td>
<td>1,2-vinyl/1,4-styrene 47.5/28/24</td>
</tr>
<tr>
<td>Impurity [wt%]</td>
<td>0.5</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>$M_w$ [kg/mol]</td>
<td>~ 800</td>
<td>260</td>
<td>450</td>
</tr>
<tr>
<td>Mooney viscosity</td>
<td>50-60 (100°C)</td>
<td>46 (125°C)</td>
<td>69 (100°C)</td>
</tr>
<tr>
<td>ML (1+4)</td>
<td>-65</td>
<td>-54</td>
<td>-20</td>
</tr>
</tbody>
</table>

It was difficult to determine the exact molecular weight of the NR using gel permeation chromatography (GPC), because there was always residual gel. Literature$^{20}$ suggests an approximate $M_w$ value of 8x10$^5$ g/mol and $M_w/M_n = 2.3$.

*Preparation of conventional EPDM nanocomposite (~ 10 wt% silica)*

The conventional nanocomposites were prepared in an internal mixer ($V = 390$ cm$^3$) with tangential rotors and a fill factor of ~ 70 vol%. The starting temperature was 50 °C and the rotor speed was adjusted to reach temperatures above 140 °C. Usually for 10 to 15 wt% silica, a rotor speed of 110 rpm was enough to achieve the desired temperature (140 - 170 °C). However, for mixture with 1 wt% silica the rotor speed was increased up to 130 rpm, because this small amount of silica does not significantly contribute to a torque increase. The actual temperature of mixing was kept at 140 - 160 °C for all compounds, regardless whether a coupling agent was used or not, in order to maintain equal processing conditions for all samples. In the presence of TESPT coupling agent the
temperature must be above 140 °C to start the silanization reaction but below 170 °C to prevent crosslinking of the rubber due to sulphur release from the coupling agent.

The mixing was performed in two steps. In the first step ZnO, stearic acid, half the amount of silica and half the amount of TESPT (if used) were added to the rubber and in the second step the remaining components were added. The mixing time of all components in the internal mixer was approximately 6 min. At the end, the so called ‘dump’ temperature of the mixture was measured. The dump temperature should be always above or equal to 140 °C to ensure that the silanization reaction is completed. The compound formulations used are shown in Table 5.2.

Table 5.2. Mixing parameters for EPDM conventional nanocomposites.

<table>
<thead>
<tr>
<th>Components [phr]</th>
<th>15 phr</th>
<th>15 phr*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(10 wt%)</td>
<td>(11 wt%)</td>
</tr>
<tr>
<td>EPDM/Keltan 512</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Silica/ZEOSIL 1165 MP</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Oil/Sunpair 2280</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Silane/TESPT</td>
<td>0</td>
<td>1.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>131</strong></td>
<td><strong>132.2</strong></td>
</tr>
</tbody>
</table>

* Coupling agent (TESPT)

* Silica content of conventional nanocomposites as determined by TGA

It should be noted, that the silica content as measured by TGA was lower than when calculated from Table 5.2. In the rubber industry, phr (parts per hundred rubber) is the commonly used unit for quantity, because it simplifies the preparation of the conventional rubber/silica nanocomposites. Further in the text reference is always made to wt% silica instead of phr. It is noted that the content of inorganics (silica and ZnO) in the conventional nanocomposites was determined by TGA (averaged over two measurements) and the silica content was obtained after subtraction of the known ZnO content. The amount of TESPT was 8 wt% with respect to the amount of silica added to the rubber. Even though the rubber compounds were not intended for vulcanization, stearic acid and ZnO were
additionally added in order to approximate the preparation conditions of industrial rubber/silica mixtures. ZnO is used as an activator and stearic acid as a plasticizer and a co-activator for sulphur vulcanization (when performed).

**Bound rubber determination**

*In-situ* and conventional rubber/silica nanocomposites with various silica amounts were immersed in THF, which is good solvent for the three rubbers. The ratio between the rubber/silica nanocomposites and the solvent was kept constant (2 % w/v) and the samples were immersed in the solvent for 48 h at room temperature while shaking. The residues were dried for 72 h at 50 °C under vacuum. The bound rubber content was calculated as following:

\[
\text{Wt}% \text{ Bound rubber content} = \frac{w_{\text{residue}} - w_{\text{silica}}}{w_{\text{original}} - w_{\text{silica}}} \times 100
\]  

where, \(w_{\text{residue}}\) is the weight of the sample after solvent treatment in (g), \(w_{\text{original}}\) is the weight of sample before solvent treatment in (g) and the \(w_{\text{silica}}\) is the weight of silica in (g) in the nanocomposite.

**Preparation of in-situ nanocomposites (NR, EPDM and SBR) in dynamic conditions via batch mixing**

Dynamic mixing was performed using a Haake Rheomix OS kneader with a 60 cm\(^3\) volume mixing chamber. The (NR, EPDM and SBR) *in-situ* nanocomposites were prepared at 80 °C in three subsequent steps, as shown in Figure 5.1.

![Figure 5.1. Schematic representation of the preparation of in-situ nanocomposites under dynamic conditions in a batch mixer.](image-url)
Prior to the reactive mixing, the chamber was isolated with a Teflon foil in order to prevent leakage of the liquid chemicals (TEOS and catalyst solution) during the sol-gel reaction. In the first step indicated in Figure 5.1, the rubber is pre-cut in smaller pieces (2 x 2 cm) and mixed in the mixer for approximately 5 min at a rotor speed (RS) of 50 rpm and a temperature of 80 °C, until a homogeneous rubber mass is obtained, as indicated by the stabile torque value (15 - 18 Nm). In the second step the TEOS is added drop-wise to the rubber in order to provide better mixing and prevent any possible leakage of the non-mixed TEOS. The time needed to obtain a homogenized rubber-TEOS mixture varied between 2 - 5 min, depending on the amount of TEOS added. The homogenized mixture of rubber and TEOS had a stabile torque value of 5 - 7 Nm. The addition of higher TEOS amounts required a longer mixing time (~ 5 min) until stabile conditions were reached. The last step is the addition of the catalyst solution needed to conduct the sol-gel reaction for silica formation. The catalyst solution (concentration 0.096 mol/l) was added in the same weight ratio 1:5 (TEOS:H₂O) as in the static conditions in order to preserve the same reaction conditions. This allows us to follow the changes occurring in the structure of the in-situ nanocomposites only as a result of the dynamic mixing.

Since the reactive mixing proceeded in the presence of a large amount of catalyst solution, the largest problem was the leakage of the solution despite the Teflon isolation. Therefore the rotor speed needed to be reduced and maintained in the range of 30 to 40 rpm in order to minimize leakage (2 - 7 wt% of the initial amount) of the catalyst solution. After the addition of catalyst solution the torque dropped to 2 Nm and remained constant during the mixing process.

The targeted three different silica contents (~ 3, 10 and 15 wt%) in the in-situ (NR, EPDM and SBR) nanocomposites were obtained by varying the reaction time between 2 - 15 min. The composition of the system used to prepare the in-situ nanocomposites with three different silica contents is shown in Table 5.3
Table 5.3. Composition of reaction mixture for obtaining in-situ (NR, EPDM and SBR) nanocomposites with various silica contents using 1:5 ratio of (TEOS:H$_2$O) at 80 °C.

<table>
<thead>
<tr>
<th>Amount of TEOS [wt %]</th>
<th>Reaction time [min]</th>
<th>Silica content [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>2</td>
<td>~ 3</td>
</tr>
<tr>
<td>33</td>
<td>10</td>
<td>~ 10</td>
</tr>
<tr>
<td>50</td>
<td>15</td>
<td>~ 15</td>
</tr>
</tbody>
</table>

**Preparation of EPDM in-situ nanocomposite via reactive extrusion**

The continuous one-step preparation of the *in-situ* nanocomposites via reactive extrusion was performed in a 30 mm diameter co-rotating twin screw extruder at Materials Science Center DSM Ahead (Geleen). The rubber used in the extrusion was EPDM Keltan 512. Prior to the processing it was ground into small flakes (~ 5 x 5 mm$^2$) and added continuously to the extruder using a gravimetric dosing unit at a constant throughput ($Q$) of 1 kg/h. A specific screw was specially designed to match the requirements for (i) performing the sol-gel reaction in extruder, (ii) efficient mixing between the rubber and the low viscous reactive liquids (TEOS and catalyst solution) particularly in the reaction zone, and (iii) longer reaction time for the silica formation. The extruder consisted of three essential zones, the rubber mixing zone, the TEOS mixing zone and the reaction zone as indicated in Figure 5.2.

![Figure 5.2. Schematic representation of the reactive extruder used in DSM for conducting a sol-gel reaction in EPDM.](image)

Two injection points were used for the dosing of the TEOS and the catalyst solution, respectively. The flow rate of both components was controlled individually and adjusted accordingly during the sol-gel reaction. The barrel
temperature was controlled via an external system and an additional thermocouple was placed at the exit of the reaction zone in order to measure the actual reaction temperature. The extruder barrel was divided into several temperature zones each provided with individual temperature control system which allowed gradual decrease of the temperature towards the reaction zone \((T = 150 \, ^\circ C)\) in order to prevent possible evaporations of the reactants.

The processing parameters of the sol-gel reaction in the extruder were:

- Reaction temperature \((T = 150 \, ^\circ C)\)
- Reaction time \(\sim \) 6 min
- TEOS amount: 25 wt\% (500 g/h)
- Amount of water: 60, 120, 240 and 360 g/h

The processing parameters that are kept constant throughout the reaction are the feed rate \(Q\), the screw speed \(N\) per experiment, and the TEOS amount. The only varying parameter was the amount of catalyst solution controlled by the injection system.

5.2.2. Characterization

Transmission Electron Microscopy (TEM)

The structure of the nanocomposites was studied using the TEM. Ultrathin sections (70 - 100 nm) were obtained using a Reichert-Jung Ultracut E microtome equipped with a diatome diamond knife for dry cutting for trimming (45° angle) and sectioning (35° angle) at a temperature of -140 °C. The sections were placed on a 200 mesh copper grid with a carbon supportive layer. The sections were examined with the TEM Sphera instrument, FEI Tecnai 20 (operating voltage of 200 kV). It should be noted, that later in the text it will be referred to structure and not morphology of the nanocomposites.

Rubber process analyzer (RPA)

The RPA is specially designed rheometer for studying the dynamic mechanical properties of rubber materials. It contains a grooved die that prevents
slippage of the material during the measurements at high strains (> 100 %). It generally measures the torque in the testing sample caused by the applied deformation. By applying a Fourier transformation the torque is divided into an elastic and viscous components that characterize the dynamic mechanical properties of the material. Measurements were performed using RPA 2000 tester from Alpha technologies at 100 °C and a frequency of 0.50 Hz. The strain sweep was performed in the range of 0.56 to 1250 % strain.

**Thermo-gravimetric analysis (TGA)**

A Q500 TGA from TA Instruments was used for the quantitative determination of the silica content in the prepared rubber/silica nanocomposites. Samples were heated in air atmosphere with 10 °C/min up to 900 °C to provide complete oxidation of the carbon. The residue after this thermal treatment is assumed to be composed only of silica. All measurements were repeated at least twice and an average of the results was used.

**5.3. Results and Discussion**

**5.3.1. Comparison of in-situ nanocomposites prepared under dynamic (using an batch mixer) and static conditions**

The conditions under which the sol-gel reactions proceed in rubber, static or dynamic, are very important in determining, i.e. the structure of the *in-situ* nanocomposites. The structure influences to a large extent the mechanical properties of the nanocomposite materials. In this part a comparison is made between the structure and the properties of the *in-situ* nanocomposites prepared under static and dynamic conditions. Therefore, *in-situ* nanocomposites were prepared employing both mixing and using the same reaction conditions, such as temperature, amount of TEOS, TEOS:H₂O ratio and reaction time of 15 min (Table 5.4).
Table 5.4. Silica content for the in-situ (NR, EPDM and SBR) nanocomposites under dynamic (and static) conditions with 1:5 ratio of (TEOS:H₂O) at 80 °C.

<table>
<thead>
<tr>
<th>TEOS amount [wt%]</th>
<th>Reaction time [min]</th>
<th>NR</th>
<th>EPDM</th>
<th>SBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>15</td>
<td>14.5</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>33</td>
<td>10</td>
<td>9</td>
<td>8.5</td>
<td>9.5</td>
</tr>
<tr>
<td>16</td>
<td>2</td>
<td>3</td>
<td>2.4</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 5.4 shows that significantly higher silica content is obtained during dynamic mixing (~ 15 wt%) as compared to the static mixing (~ 1.5 - 5.5 wt%) for the same reaction time of 15 min. The increase in silica content for the dynamically prepared *in-situ* nanocomposites is ~ 400, ~ 800 and ~ 200 % for NR, EPDM and SBR, respectively. It should be noted, that there is discrepancy in the amount of TEOS in the EPDM *in-situ* nanocomposite prepared under dynamic and static conditions. The reason is that 33 wt% is the maximum amount of TEOS in EPDM at 80 °C under static conditions. This may represent an advantage for the dynamic mixing because it allows the use of a higher amount of TEOS than possible under static conditions.

Achieving higher silica content under dynamic conditions for the same reaction time can be ascribed to the mixing effect that allows formation of so-called renewable interfaces. These interfaces enable more frequent interaction between the TEOS-swollen rubber and the catalyst solution during the sol-gel reaction. Thus for the same reaction time under dynamic conditions *in-situ* nanocomposites with higher silica content are obtained. Depending on the mixing efficiency, the frequency and the thickness of these interfaces is expected to significantly influence the silica content, particle size and dispersion throughout the matrix.

While under static conditions the sol-gel reaction is strongly affected by the diffusion of the TEOS and the catalyst solution through the sample, under dynamic
conditions this problem can be surpassed by the formation of these interfaces. The structures of the obtained NR, EPDM and SBR in-situ nanocomposites under dynamic conditions are shown in Figure 5.3.

![Figure 5.3. Structure of in-situ NR, EPDM and SBR nanocomposites prepared under dynamic conditions (reaction time of 15 min at 80 °C with 50 wt% TEOS) with 14.5, 14 and 15 wt% silica, respectively. The silica regions and aggregates are indicated with the arrows and the area with only single particles indicated in the frame.](image)

Figure 5.3 shows a non-uniform distribution of the silica particles throughout the rubber matrix indicating regions in which silica particles are tightly packed, silica aggregates and single particles. The silica regions have irregular spherical shapes with approximate sizes ranging from 0.2 to 6 μm and sometimes even larger. These regions are observed in all in-situ (NR, EPDM, and SBR) nanocomposites also at lower silica contents (~ 3 wt%) but strongly emphasized at higher silica loadings (~ 15 wt%).

The non-uniform structure of the dynamic in-situ nanocomposites can be ascribed to the inefficient mixing between the swollen rubber and the catalyst solution during the sol-gel process. The very low shear forces in the batch mixer are not able to provide good mixing during the sol-gel process, as a result of which silica regions and aggregates are formed. The silica regions resemble to trapped catalyst droplets inside the swollen rubber matrix in which silica preferably forms. This structure is rather different than the one observed in the in-situ nanocomposites prepared under static conditions (see Figure 2.8 in Chapter 2) and
also no silica gradient is expected under dynamic conditions as diffusion is no longer a controlling factor for the sol-gel reaction. Therefore, RPA measurements were performed and the moduli ($G'$) of the EPDM in-situ nanocomposites prepared under static and dynamic conditions are determined, as shown in Figure 5.4.

![Figure 5.4](image)

**Figure 5.4.** (a) Comparison of the $G'$ modulus at $\sim 10$ % silica content between EPDM in-situ nanocomposites prepared under static (reaction time of 10 h with 33 wt% TEOS) and dynamic conditions (reaction time of 10 min and 33 wt% TEOS) at 80 $^\circ$C and (b) the $G'$ at low (2%) and high (200 %) strain.

The results in Figure 5.4 show that the $G'$ modulus of the in-situ nanocomposites prepared under dynamic conditions has somewhat lower value at low and higher strain, as compared to the in-situ nanocomposite prepared under static conditions. As discussed in Chapter 4, the in-situ nanocomposites prepared under static conditions show an interesting behaviour (when compared to the conventional nanocomposites) which contradicts the common belief that a higher modulus at low strain is as a result of non-uniform dispersion of the silica aggregates in the rubber.\textsuperscript{21-24} The in-situ nanocomposites prepared under static conditions showed higher modulus at low strain and this was ascribed to several factors: (1) uniform dispersion of small size silica particles which provides a large surface area available for interaction with the rubber matrix, (2) the hydrophobic surface of the in-situ silica caused by the presence of ethoxy groups and hexylamine, which promotes stronger rubber-silica interactions, (3) the formation of trapped entanglements\textsuperscript{25,26} by anchoring of the rubber chains on the silica surface that
ultimately is responsible for modification of the entanglement density of the entire rubber matrix resulting in higher stiffness and (4) the higher bound rubber content.\textsuperscript{27} On the other hand, the modulus at high strain was mainly assigned to the strength of the rubber-silica interactions.\textsuperscript{28,29} In the absence of filler-filler network, the drop in the modulus (Payne effect) in the \textit{in-situ} nanocomposite is due to the disentanglement of the trapped entanglements that begin to slip and detach from the silica surface, intensifying further with the increase in strain.

In the case of the dynamic \textit{in-situ} nanocomposites a contribution of all factors mentioned to the modulus at low and high strain is expected. As compared to the static \textit{in-situ} nanocomposites, lower modulus at low and high strain are obtained for the dynamically prepared nanocomposites, which is probably due to the non-uniform silica dispersion (see Figure 5.3) and the relatively low surface area available for interaction with the rubber matrix. This consequently results in a decreased particle effect on the entanglement density of the rubber network leading to lower stiffness. Additionally, the bound rubber content for the \textit{in-situ} nanocomposite under dynamic conditions is also lower (see Table 5.5), being only 7.7 wt\% as compared to the one obtained for the static \textit{in-situ} nanocomposites (33 wt\%) (see Table 4.8 in Chapter 4). Moreover, the particle size, known to have significant influence on the reinforcement, is somewhat larger for the dynamic \textit{in-situ} nanocomposites as compared to the static \textit{in-situ} nanocomposites (Figure 5.5).
Figure 5.5. Comparison of single particle sizes (no aggregates considered) between the NR, EPDM and SBR in-situ nanocomposites prepared under static (Figure 2.8, Chapter 2) and dynamic conditions (Figure 5.3) for reaction time of 15 min at 80 °C with the corresponding silica contents.

The silica contents of the corresponding in-situ nanocomposites (static and dynamic conditions) in Figure 5.5 are shown in Table 5.4. It should be noted, that for the particle size measurements in the dynamically prepared in-situ nanocomposites only the isolated single particles were considered, excluding the ones in the silica regions and aggregates due to difficulty to distinguish separate particles. The general observation is that the in-situ nanocomposites prepared under dynamic conditions resulted in somewhat larger particle sizes and polydispersity, particularly in the case of EPDM nanocomposites where particle sizes were found to range between 25 and 90 nm. The larger particle size and the polydispersity in the dynamically prepared nanocomposites can be ascribed to the mixing effect. As a result of the renewable interfaces during the mixing, an already growing particles may repetitively be exposed to additional fresh catalyst solution that enables them to grow to larger sizes, unlike other particles that eventually remain smaller.

Interestingly, the particle size in the SBR nanocomposite decreased significantly from approximately 95 nm for the static conditions to 25 nm average size for the dynamic conditions. A possible explanation could be the more preferred localized silica formation in the SBR matrix in the mentioned silica regions. In these localized regions the amount of available catalyst solution is shared by a large
number of surrounding particles which renders growth of the silica particles to larger sizes (see Figure 5.3). It was noted earlier that the swelling of SBR in TEOS under static conditions is limited to 50 wt% of TEOS because beyond this amount SBR starts to dissolve significantly. No such problem was encountered during the dynamic mixing (no leakage of TEOS or dissolved SBR).

5.3.2. In-situ nanocomposites prepared in dynamic conditions via batch mixing vs. conventional nanocomposites

The properties of the obtained in-situ nanocomposites under dynamic conditions were evaluated in comparison to the conventional nanocomposites (with and without coupling agent) at approximate 10 wt% silica loading, by conducting RPA measurements, of which the results are shown in Figure 5.6.

Figure 5.6. Comparison of the modulus ($G'$) of in-situ EPDM (reaction time of 10 min at 80 °C with 33 wt% TEOS) and conventional (with and without coupling agent) nanocomposites at approximate silica loading of 10 wt%.

Figure 5.6 suggests a higher modulus ($G'$) of the in-situ EPDM nanocomposite at high and low strain (~ 30 % increase) as compared to the conventional nanocomposite (with and without coupling agent). However, despite the non-uniform silica dispersion, the in-situ NR, EPDM and SBR nanocomposites prepared under dynamic conditions showed a higher modulus at low (2 %) and high
strain (~200 %) as compared to the conventional ones (Figure 5.7).

Several factors can be considered to explain this behaviour of the in-situ nanocomposites. The areas where silica is uniformly distributed (see TEM images in Figure 5.3) still provide somewhat larger surface area available for interaction with the rubber which in combination with the hydrophobic surface of the silica particles (shown in Chapter 4), the trapped entanglements and the trapped rubber chains (Figure 4.16) results in more extensive modification of the entanglement density of the rubber matrix, resulting in higher modulus at low and high strain for the dynamically prepared in-situ nanocomposites. The bound rubber as a direct consequence of these factors obtained for both, conventional and in-situ dynamic, nanocomposites is shown in Table 5.5.

<table>
<thead>
<tr>
<th>~10 wt% silica</th>
<th>In-situ</th>
<th>Conventional</th>
<th>Conventional+CA</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>13.9</td>
<td>38</td>
<td>51.2</td>
</tr>
<tr>
<td>EPDM</td>
<td>7.7</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>SBR</td>
<td>0</td>
<td>15.2</td>
<td>36.5</td>
</tr>
</tbody>
</table>

The results in Table 5.5 show a lower bound rubber content for the dynamic in-situ nanocomposites as compared to the conventional. The reason for the lower bound
rubber content can be ascribed to the non-uniform silica distribution (localization in particular regions) and the relatively large silica particles. It should be noted, that the SBR in-situ nanocomposite always resulted in complete extraction of the rubber and no bound rubber content was obtained. A few possible reasons that can explain this phenomenon were elaborated in Chapter 2. However, for the SBR conventional nanocomposites (with and without coupling agent) a certain bound rubber content was obtained. It is expected that the occluded rubber contributes additionally to the bound rubber content and consequently to the modulus.

The so-called occluded rubber\textsuperscript{30} is commonly observed in conventionally prepared nanocomposites. It is a rubber that is trapped in the voids of the silica aggregates or between the aggregates and behaves as immobilized, adopting the behaviour of the solid particles. This is valid not only for SBR but also for the NR and EPDM conventional nanocomposites.

While for the static in-situ nanocomposites it was easy to separate the effect of the single particles and the aggregates, and to clearly define the high modulus at low and high strain, in the dynamic in-situ nanocomposites this is not so straightforward, because not only silica particles but also aggregates and silica regions are observed. This makes the interpretation of the factors responsible for the modulus at low strain rather ambiguous. As observed from the previous results, both the single particle effect and the non-uniform silica dispersion increase the modulus at low strain.

In summary, we believe that the single silica particles in the dynamically prepared in-situ nanocomposites and the trapped entanglements caused by the good rubber-silica interactions contribute to the high modulus \((G')\) at low strain, as compared to the conventional nanocomposites. At high strain the modulus of the in-situ nanocomposites remains higher due to the unique surface chemistry of the in-situ silica and the possibility of having trapped rubber chains in the silica structure.
5.3.3. Effect of amount of water on the sol-gel reaction during dynamic mixing

The large amount of water (catalyst solution) used during the dynamic mixing is always a problem when efficient mixing is concerned. Therefore, different TEOS:H₂O ratios were probed and their effect on the structure of the obtained nanocomposites announced. Stoichiometrically, the sol-gel reaction does not require high amounts of water as shown by the overall reaction:

\[ Si(OR)_4 + 2H_2O + catalyst \rightarrow SiO_2 + 4ROH \]

The theoretical amount of water and silica content is calculated from the stoichiometric ratio of these two components with TEOS, where 1 mol of TEOS corresponds to 2 mol of water and 1 mol of silica. From the calculation, full conversion of 50 wt% of TEOS into 22.3 wt% theoretical silica can be achieved with only 14 wt% water. We varied the ratio TEOS:H₂O from 1:5 to 1:0.25 and obtained nanocomposites via dynamic mixing, with different silica contents, as shown in Figure 5.8.

**Figure 5.8.** (a) Silica content of in-situ EPDM nanocomposite (reaction time of 15 min at 80 °C with 50 wt% TEOS) for different TEOS:H₂O ratio, (b) conversion of TEOS during the dynamic mixing.

<table>
<thead>
<tr>
<th>wt% Theoretical silica</th>
<th>TEOS:H₂O</th>
<th>wt% Experimental silica</th>
<th>TEOS [%] conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.3</td>
<td>14</td>
<td>22.3</td>
<td>100</td>
</tr>
<tr>
<td>22.3</td>
<td>250 (1:5)</td>
<td>15</td>
<td>67</td>
</tr>
<tr>
<td>22.3</td>
<td>50 (1:1)</td>
<td>12</td>
<td>54</td>
</tr>
<tr>
<td>22.3</td>
<td>25 (1:0.5)</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td>22.3</td>
<td>12.5 (1:0.25)</td>
<td>7</td>
<td>31.4</td>
</tr>
</tbody>
</table>

Figure 5.8 suggests that decreasing the catalyst solution from 1:5 (used until now for all experiments) to 1:0.25 of TEOS:H₂O, the silica content decreased from 15 to 7 wt%. A higher concentration of catalyst solution enhances both, the hydrolysis
and the condensation reaction resulting in a higher silica content and thus a higher TEOS conversion (see Figure 5.8 (b)). This was also reported by earlier studies \textsuperscript{31,32} where a similar behaviour was observed with the increase of water amount and the catalyst concentration. The reason for the large discrepancy between the theoretically predicted and the experimentally obtained silica content, even for the highest catalyst amount, can be partially ascribed to the poor mixing between the TEOS-swollen rubber and the catalyst solution in the batch mixer and the relatively short reaction time of 15 min.

In summary, the disadvantages of the \textit{in-situ} nanocomposites prepared in a batch mixer are the particle polydispersity and the non-uniform silica dispersion caused by the inefficient mixing. The reaction temperature of maximum 80 °C is limited by the boiling temperature of the water. However, the greatest advantages of the dynamic mixing are the significantly increased silica content (as compared to \textit{in-situ} static nanocomposites) obtained for the same reaction time and also the possibility to use lower amount of water. This suggests that industrial production of the \textit{in-situ} nanocomposites under dynamic conditions, such as in extrusion, under high reaction temperatures, lower water content and extensive mixing would be possible.

\textbf{5.3.4. Reactive extrusion}

In general, twin-screw extruders provide improved mixing as compared to the single-screw extruders. Twin-screw extruders are commonly used in the industry for performing reactive extrusions, such as polymerizing of new polymers, modifying polymers by graft reactions and blending different polymers.\textsuperscript{2} Therefore, in the following paragraph a reactive extrusion for preparation of \textit{in-situ} nanocomposites via sol-gel reaction will be elaborated.

After obtaining homogenized rubber melt in the first zone (see Figure 5.1), the TEOS was injected at a constant flow rate of \( \sim 500 \text{ g/h} \). The mixing of TEOS and the rubber melt is successfully performed for a (residence) time of 2 min with no back flow evaporation. The addition of TEOS reduced the rubber viscosity and
enabled better temperature control in this zone. Since the sol-gel reaction generally involves the use of large amounts of water (catalyst solution), the control of the amount of water and its maintenance in a liquid state inside the extruder represented the largest challenge in this process. In order to keep the water in liquid state at $T = 150 \, ^\circ\text{C}$, the pressure had to be kept between 5 - 10 bar to prevent water evaporation in the extruder. The high pressure in the extruder was achieved with melt seals at several locations in the extruder. It is important to keep the water in liquid state because of the mechanism according to which we believe the sol-gel reaction proceeds. Namely, via inverse micelles formed in the rubber matrix where hexylamine (catalyst) encloses the water in the inverse micelle and behaves also as surfactant. If the water is in gas state, the transformation of water into the swollen rubber (via inverse micelles) would be impeded with no clear effect on the silica formation.

During the present experiments, the optimal screw speed was found to be 150 rpm. Decreasing the screw speed affected the pressure inside the extruder, causing evaporation of the water (catalyst solution) due to failing of the melt seals, and by increasing the screw speed the temperature and the pressure also increased, leading to destabilization of the system. For a constant amount of TEOS of ~ 500 g/h, the amount of catalyst solution was gradually increased from 60, 120, 240 to 360 g/h avoiding destabilization of the system and allowing the process always to adjust to the new conditions for approximately 20 - 30 min before the water content was increased again. The highest amount of water achieved with stable conditions was 360 g/h (see Figure 5.9).
The pressure in the TEOS mixing zone and the reaction zone was monitored via the injection systems used for dosing of these liquids. The reaction temperature measured from the thermocouple was always in the range of 150 - 160 °C which corresponded to the set temperature of the barrel in that zone. The reaction time of the sol-gel reaction time was approximately 6 min and for 360 g/h it resulted in formation of 3.2 wt% silica in the EPDM rubber (as determined by TGA). During the reactive extrusion no distinct odour from the ethanol removed during the sol-gel reaction was detected, probably because the amount of silica formed was relatively low.

5.3.4.1. Structure of the extruded in-situ nanocomposite and the effect of mixing

The structure of the *in-situ* nanocomposite obtained via reactive extrusion is shown in Figure 5.10.
Figure 5.10. Structure of (a) extruded nanocomposite, $t = 6$ min in comparison to (b) nanocomposite in static condition, $t = 15$ min for TEOS amount of 50 wt% TEOS at 150 °C and (c) particle size distribution in extrusion and static conditions.

The TEM image of the extruded nanocomposite in Figure 5.10 (a) suggests a relatively uniform dispersion of the silica particles throughout the rubber matrix with no pronounced aggregation or presence of silica regions (see Figure 5.3), indicating a significantly more efficient mixing than in the batch mixer. The extruded nanocomposite showed enhanced particle polydispersity and very large particle sizes reaching more than 300 nm.

Triggered by this interesting result, initially it was expected the high temperature (150 °C) to be responsible for the large particle sizes in the extruded nanocomposite. In order to support this hypothesis the same experiment was performed under static conditions keeping the temperature and the TEOS amount same as in the extrusion. The TEOS:H$_2$O ration was 1:2 instead of the one used during the extrusion (1:0.72) because from practical reasons the amount of catalyst solution was too low and could not cover the swollen rubber sample. The reaction time was extended to 15 min, instead of the 6 min for extrusion, to make sure that particles have enough time to grow. To our surprise, despite the longer reaction time and larger amount of catalyst solution, the average particle size in the nanocomposite prepared under static condition was 45 nm with very low polydispersity (see Figure 5.10 (b) and (c)).

Due to the high reaction temperature the sample was prepared in special glass vial that can sustain pressures until approximately 3 bar. The temperature - pressure
diagrams\textsuperscript{33} suggest minimum 5.5 bar pressure in order to keep the water liquid at temperatures of 150 °C. A possible explanation for the smaller particle size in the \textit{in-situ} static nanocomposite might be the partial evaporation of the catalyst solution in the vial, thus reducing the amount of water and catalyst available for silica formation in the rubber. The particles in the extruded nanocomposite grew almost 10 fold larger when compared to the static experiment. To explain this the following three reasons were consider: the renewable interfaces caused by the extensive mixing, the very high pressure inside the extruder and the melted rubber mass. The intensive shear forces between the swollen rubber and the catalyst solution caused by the screws can enable formation of interfaces with very small thickness which to some extent removes the diffusion limitations present for the static conditions.

In order to show that diffusion limitations may be neglected for very small thicknesses an experiment was performed, where the sol-gel reaction proceeded in EPDM samples with different thickness (0.12, 0.8 and 2 mm). The conditions were approximated to the ones during the extrusion: 25 wt\% of TEOS, TEOS:H$_2$O = 1:2 for all samples at $T = 150$ °C and reaction time of 6 min. The reaction was performed in special pressure vials ($P_{\text{max}} \sim$ 3 bar). The particle size determined on the surface and the centre in the \textit{in-situ} nanocomposites, as observed by TEM is shown in Figure 5.11.
Figure 5.11. *In-situ* EPDM nanocomposites with different thickness (0.12, 0.8 and 2 mm) prepared in static conditions for 6 min reaction time at 150 °C with 25 wt% TEOS.

Figure 5.11 shows that for very small thicknesses (0.12 mm) there is no gradient in silica particle size which indicates that the diffusion of the TEOS and the catalyst solution under such extreme temperature conditions (150 °C) proceeds fast. As the thickness is increased to 0.8 and 2 mm, gradient is observed, resulting from the non-uniform distribution of the TEOS and the catalyst solution along the sample thickness during the sol-gel reaction. The small average particle size for the three *in-situ* nanocomposites on the surface (13 - 14 nm) is probably due to the partial evaporation of the catalyst solution preventing them to grow to larger sizes.

This might indicate that indeed the efficient mixing during the extrusion provides thin interfaces between the swollen rubber and the catalyst solution that surpasses the diffusion limitations. During the mixing process it is expected that these interfaces are continuously renewed with fresh catalyst solution which may explain the large silica particles. In addition, the large particle size can be also ascribed to the relatively high pressures in the extruder required to keep the catalyst solution in liquid state. It was suggested by earlier studies\textsuperscript{34,35} that higher pressures might accelerate the polycondensation rate without altering the mechanism of the silica formation. It is believed that the increase in the polycondensation rate is a direct consequence of the volume contraction caused by the increased pressure that might ultimately lead to larger particle sizes.
Moreover, the growing silica particles during the extrusion process are expected to have less (if any) restrictions from the rubber chains. The intensive mixing in the extruder stretches and loosens the rubber chains in the molten TEOS-swollen rubber, allowing the particles to possibly grow to larger sizes without much spatial restrictions. Under static conditions, the particle size could be to some extent limited by the entangled chains in the rubber network, because the silica particles must push the rubber chains away while growing.

The effect of the particle size and the polydispersity on the reinforcement of the extruded nanocomposite, as compared to the in-situ nanocomposite prepared in the batch mixer and the conventional nanocomposite (with coupling agent) for same silica content is shown in Figure 5.12.

![Figure 5.12. Comparison between the (a and b) extruded nanocomposite, (a) the in-situ nanocomposite prepared in batch mixer and (b) the conventional nanocomposite with coupling agent (CA) (10 wt % silica), (c) Moduli ($G'$) at low and high strain and (d) Structure of the extruded, in-situ and conventional (+ CA) nanocomposite, respectively.](image)

Figure 5.12 (a), shows lower modulus at low strain for the extruded nanocomposite as compared to the in-situ nanocomposite prepared under dynamic conditions and
comparable modulus at high strain for both materials, *in-situ* and conventional. The silica dispersion in the *in-situ* EPDM nanocomposite prepared in an batch mixer, at low silica content of 2.4 wt%, is noticeably better than at higher silica contents (see Figure 5.3), showing a higher presence of single particles and significantly less aggregates or silica regions. This resulted in a higher modulus at low and high strain (see Figure 5.12 (c)).

To our surprise, the modulus of the extruded sample (3.2 wt% silica) was found to be similar to that of the conventional nanocomposite with three times more silica (10 wt%) including coupling agent. This indicates that the *in-situ* nanocomposites, produced via a continuous industrial process like reactive extrusion, are able to provide similar or even better reinforcement at much lower silica loadings, acknowledging the effect of the single silica particles. Moreover, their enhanced hydrophobic nature is also expected to give additional rise to the modulus, particularly at high strain when rubber-silica interactions play important role.

**5.4. Conclusions**

The preparation of the *in-situ* nanocomposites under dynamic conditions provided significant increase in silica content for the same reaction time. The obtained nanocomposites consisted of somewhat larger silica particles with pronounced polydispersity and aggregation. Due to the mixing a gradient in particle size was not observed, as under static conditions. It was shown that the sol-gel reaction in rubber via reactive extrusion is possible and that it has potential to allow a one-step production of *in-situ* nanocomposites with promising mechanical properties. By changing the reaction conditions (mixing, higher $T$) a significant improvement in the reaction time of the sol-gel reaction we achieved, from 24 - 72 h reported in literature to 6 min in extruder. One must be aware, that nanocomposites with higher silica content are required for better performance. The reactive extrusion is a complex process that involves many aspects that need to be further addressed. Some of those are: tuning of the screw design to provide good
mixing and longer reaction time, better control over the pressure and the amount of water used during the reaction and larger throughput which will eventually enable production of nanocomposites for various applications via reactive extrusion.
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Technology assessment

The 21st century gave birth to the nano-science as one of the fields contributing to a high level of scientific and technological development. Hybrid organic-inorganic materials play a major role in the development of advanced functional materials. In addition to the high versatility in chemical and physical properties, hybrid nanocomposites present paramount advantage because they can combine integration and miniaturization, therefore opening promising applications in many fields: optics, electronics, ionic’s, mechanics, membranes, coatings and medicine.¹

So far conventional rubber nanocomposites are produced via a time and energy consuming process of mixing rubber and silica. The transformation into a continuous process such as the extrusion will enable bulk production of conventional nanocomposites.² However, the use of extrusion to produce nanocomposites is difficult due to the agglomeration of the inorganic phase (particularly for nano-size fillers), rendering good dispersion into the rubber phase. Therefore, it remains a need for a method capable of increasing the compatibility
and productivity of conventional nanocomposites by overcoming the current limitations. Two possible approaches are considered as a possibility to improve the compatibility and the productivity of the future rubber/silica nanocomposites.

6.1. Surface chemistry of the in-situ silica particles

So far the greatest challenge in the rubber industry was the improvement in compatibility between the silica, being strongly polar and the rubber, being strongly apolar. In Chapter 4 with the help of Solid-state NMR a unique structure of the *in-situ* silica was revealed, made via sol-gel reaction using hexylamine as catalyst. The NMR study revealed so-called ‘hairy’ silica particles with enhanced hydrophobic character due to the presence of remnant ethoxy groups and hexylamine residing on the silica surface. Unlike the, conventional nanocomposites where the use of coupling agents is a necessity, the *in-situ* silica with its unique surface chemistry has better compatibility with the rubber in the absence of coupling agents and has consequently improved mechanical properties.

6.1.2. Future outlook and optimization

An interesting approach to further explore and tune the surface chemistry, thus the hydrophobicity of the ‘hairy’ silica particles, is by changing the silica precursor (e.g. from tetramethyl-ortosilicate-TMOS to tetrabutyl-orthosilicate-TBOS), as schematically shown in Figure 6.1.

![Figure 6.1 Schematic drawing of possible different surface chemistry of the silica particles formed via sol-gel reaction as function of the silica precursor, (a) TMOS, (b) TEOS and (c) TBOS, respectively.](image)
The schematic representation of the three possible silica surfaces for TMOS, TEOS and TBOS can possibly result in silica particles with different hydrophobicity, likely the lowest for the TMOS and the highest for the TBOS precursor. This can be ascribed to the different length of the alkoxide group residing on the silica surface, where longer chains (TBOS) are expected to provide better shielding of the hydroxyl groups and consequently increase the hydrophobic character of the in-situ silica.

The particular surface chemistry obtained for the in-situ silica is expected to provide better compatibility with the rubber matrix and to lead to easier and more efficient dispersion of the silica particles without the addition of coupling agent. The in-situ silica particles can possibly be mixed not only with rubber materials but also with thermoplastics such as: polyethylene (PE), polypropylene (PP), poly (methyl-methacrylate) (PMMA) and many others, thereby broadening its application areas.

6.2. Sol-gel reaction in rubber via reactive extrusion

Reactive extrusion can be a way to do synthesis, dispersion and functionalization of the silica particles in the prepared nanocomposites in a one-step via the sol-gel reaction. In Chapter 5 the possibilities of performing the sol-gel reaction in rubber via one-step extrusion were discussed. The attempt to perform the sol-gel reaction (in rubber) via reactive extrusion was successful and an in-situ EPDM nanocomposite with 3.2 wt% silica was obtained. The kinetic study in Chapter 4 performed with time-resolved SAXS and MAS-NMR showed that indeed the reaction rate increases significantly with temperature leading to fast formation of the silica structure (high $Q^3:Q^4$) in only 15 min. Showing the possibilities for performing the sol-gel reaction via reactive extrusion at extreme reaction conditions (high temperature and short reaction times) without really compromising the structure of the formed silica particles. The reactive extrusion has certainly its own advantages and disadvantages, such as:
Advantages:
- Easy transport of the polymer mass
- No evaporation of volatile chemicals (ethanol, TEOS and catalyst solution)
- Short residence time and mass production of the *in-situ* nanocomposites
- Good silica dispersion without time/energy consuming mixing steps

Disadvantages:
- Rather complicated process that still requires optimization (screw design, temperature, extruder configuration and dozing)
- Relatively low TEOS conversion
- High silica precursor costs
- Additional drying step of the produced *in-situ* nanocomposites to remove the remnant chemicals (ethanol, non-reacted TEOS and water)

### 6.2.1. Future outlook and optimization

The extrusion process shows great potential for production of the *in-situ* nanocomposites. However, future optimization is important for achieving higher silica content and improving the overall stability of the process. There are several parameters that can be tuned for better optimization, such as: screw speed, temperature and screw design. In general, by increasing the screw speed the mixing efficiency between the TEOS swollen rubber and the catalyst solution is increased, however one must realize that, in that case, the system is prone to destabilization.

The screw design plays an essential role in the mixing efficiency between the high viscosity rubber material and the low viscosity catalyst solution. A proper screw design should prevent back-flow evaporation and be able to maintain sufficiently high pressure in the extruder to keep the water liquid.

### 6.2.2. Side-feeding extruder

A longer reaction time is important for providing higher silica content. This
can be achieved by assembling an additional side-feeding extruder that can provide mixing of the rubber and the TEOS (short mixing time) and continuously feed this material into the second extruder used for conducting the sol-gel reaction. This allows individual controlling of each reaction parameter (temperature, screw design, screw speed and chemistry) and provides much longer reaction time required for achieving higher silica content. It should be noted that the greatest challenge in performing the sol-gel reaction in rubber via reactive extrusion is the high amount of water used during the silica formation. Two possible options are considered to surpass this problem, i.e. the use of latex in the case of NR and the use of pre-hydrolyzed TEOS (PAOS).

- **NR latex**

One way to avoid the problems with the use of high amounts of water is to use a NR latex instead of solid rubber. This can be advantageous because the rubber latex usually consists of approximately 35% solid rubber and the rest is water. Therefore, the use of additional water is not necessary which provides excellent opportunity for performing the sol-gel reaction.³

- **Pre-hydrolyzed TEOS poly (ethoxyorthosilicate) (PEOS)**

Another possibility to increase the silica content in the in-situ nanocomposites and to simplify the processing conditions is the use of a pre-hydrolyzed form of the TEOS (PAOS),⁵ as shown in Figure 6.2.

![Image](image.png)

*Figure 6.2. Pre-hydrolyzed form of TEOS (PAOS).*

Oligomeric precursors are desirable when it is necessary to increase the silica
content. It would be very interesting to conduct a study of the sol-gel reaction in presence of PAOS and hexylamine, as catalyst, for variety of thermoplastic and rubber materials.
6.3. References

[5] X. Zhu et al., Polymer Preprints; 47(2); 1133; 2006
[6] Q. Dou et al., Journal of Sol-Gel Science and Technology; 48; 51-60; 2008
Acknowledgments

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Tetic znajeki deka si tuka sekogas mi bilo polesno, za celata podrsk dodeka sum tuka I za
nasite dolgi razgovori na telefon. Juki src ti definitivno mi go razubavuvas denot, nikogas ne zaboravas da mi pises I da me potsetis da kupam shejk. Fala mnogu na site sto ve imam vo mojot zivot, najmili moi! Golemo fala na mojata najdobra drugarka Stance I na Annc vo Skopje, za prekrasniot provod sekogas koga ke se vratam I za vasat podraska da istraam vo se sto ke naumam.
Curriculum Vitae

Elena Miloskovska was born on 3 April 1980 in Skopje, Macedonia. After finishing her secondary education at the Chemistry school, ‘Marija Kiri-Skolodovska’ in 1998, she received her BSc degree in Polymer Engineering at the University of Technology and Metallurgy in Macedonia on February 2004. From March 2004 until July 2006 she was working in a Printed Circuit Board (PCB) company, Hi-Tech Corporation, as process engineer and later as a shift production manager in Skopje, Macedonia. In August 2006 the author received full scholarship from the Eindhoven University of Technology for pursuing the Master program in Polymers and Composites. She obtained Master’s degree in 2008 after completion of her thesis: ‘Structure-Property relationships of (poly)pentadecalactone (PPDL)’ in the ‘Polymer Technology’ group of prof.dr. P.J. Lemstra. In September 2008, she started her PhD study in the same group. During the PhD study, she completed three modulus of the course ‘registered Polymer Scientist’ (RPK), organized by the ‘National Dutch Graduate School of Polymer Science and Technology’ (PTN), which includes Polymer Physics, Polymer Properties, and Rheology & Polymer Processing.
List of publications

1. E. Miloskovska, D. G. Hristova-Bogaerds, C. Friedrich, M. R. Hansen, M. van Duin, G.de With
‘Growth mechanism of in-situ silica and kinetics of sol-gel reaction in rubber matrix using SAXS and Solid-State NMR’, in submission for *Macromolecules*

2. E. Miloskovska, D. G. Hristova-Bogaerds, C. Friedrich, M. R. Hansen, M. van Duin, G.de With
‘Novel ‘hairy’ silica particles with hydrophobic surface’, in submission for *Advanced Materials*

3. E. Miloskovska, D. G. Hristova-Bogaerds, C. Friedrich, M. R. Hansen, M. van Duin, G.de With
‘Structure of the in-situ silica and its effect on the properties of rubber/silica nanocomposites’, in submission for *Macromolecules*

4. E. Miloskovska, D. G. Hristova-Bogaerds, M. van Duin, A. Spoelstra, E. Niels, G.de With
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5. E. Miloskovska, D. G. Hristova-Bogaerds, M. van Duin, P. Elemans, G.de With
‘Rubber/silica nanocomposites via reactive extrusion’, in preparation for *Nanotechnology*