Membranes via particle assisted wetting

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Bibliographische Beschreibung und Referat

Membranen über partikelassistierte Benetzung

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Stichworte: partikelassistierte Benetzung, Partikel, poröse Membranen, asymmetrische Membranen, Gasseparationsmembranen, Mikrosiebe


Um die mechanische Stabilität von porösen Membranen zu erhöhen spreitet man eine Mischung aus Kieselgelpartikeln und einem Öl auf einem Vliesstoff, der mit Wasser getränkt ist. Das Aushärten des Öls und die Entfernung der Partikel führt zu einer porösen Membran, die an die Fasern der Stützstruktur angeheftet ist. Durch die inhomogene Oberfläche des Vliesgewebes sind die daran angehefteten Membranen gewellt.

Um eine ebene Stützstruktur zu erhalten, werden Mischungen aus dem Öl und Glaskugeln mit einem Durchmesser von 75 µm verwendet. Das Aushärten des Öls und die Entfernung der Partikel führt zu ebenen porösen Membranen mit Porendurchmessern im Mikrometerbereich.


Durch langsames Entfernen der Kieselgelpartikel aus der gemischten Schicht, die auf der Wasseroberfläche schwimmt, kann man in einem Zwischenstadium Kieselgelsringe erhalten.

Abstract

Membranes via particle assisted wetting

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Keywords: particle assisted wetting, particle, porous membranes, asymmetric membranes, gas separation membranes, microsieve,

Spreading of mixtures of oil with suitable silica particles onto a water surface leads to the formation of composite layers in which particles protrude at the top and at the bottom from the oil. Solidification of the oil and removal of the particles give rise to porous membranes. Pore widths and membrane thicknesses depend on particle sizes and usually are in the range of 70 – 80% of their diameters. Often freely suspended porous membranes are too fragile to operate them in pressure filtration without supportive structure.

To improve mechanical stability of porous membranes, a mixture of silica particles with an oil is spread onto a nonwoven fibrous support that was drenched with water. Solidification of the oil and removal of particles yields porous membrane attached to the fibers of the support. Due to inhomogeneous surface of the fabric, the membranes that are attached to it are corrugated.

To obtain flat supportive structures, glass beads with 75 µm in diameter are spread onto the water surface with the oil. Solidification of the oil and then removal of particles gives rise to porous membranes with pore diameters in micrometer range.

Another concept of improvement of mechanical stability is the preparation of asymmetric membranes via spreading of a mixture of two sorts of particles with opposite surface properties with the oil onto the water surface. After solidification of the oil and removal of particles, membranes with pores width in the range from 30 – 50 nm are obtained.

Slow removal of silica particles from composite monolayer that floats on the water surface gives rise to silica rings in intermediate stages of removal.

Mixed matrix membranes with embedded carbon molecular sieves are prepared in a similar process as detailed above by using carbon particles instead of silica. Carbon molecular sieves protrude at the top and bottom from the polymeric matrix. Theoretical prediction of permeability and selectivity through these membranes are much higher than in membranes where particles are smaller than the membrane thickness.
# Table of contents

Bibliographische Beschreibung und Referat ................................................... ii

Abstract ........................................................................................................ iii

List of Abbreviations ................................................................................... vii

1. **General introduction and outline of this thesis** ........................................ 1
   1.1 References .......................................................................................... 9

2. **Porous membranes on supportive structure** ............................................. 10
   2.1 Introduction ......................................................................................... 10
   2.2 Membrane preparation ...................................................................... 12
   2.3 Conclusions ....................................................................................... 22
   2.4 Experimental part ............................................................................. 23
      2.4.1 Particle preparation ..................................................................... 23
      2.4.2 Preparation of membranes attached to the fleece via decreasing of the water level ................................................... 24
      2.4.3 Preparation of membranes of the wetted fleece ......................... 25
   2.5 References ......................................................................................... 26

3. **Porous membranes with pores in micrometer range** ................................. 27
   3.1 Introduction ......................................................................................... 27
   3.2 Membrane preparation ...................................................................... 31
   3.3 Conclusions ....................................................................................... 38
   3.4 Experimental part ............................................................................. 39
      3.4.1 Preparation of glass beads coating .............................................. 39
### Table of contents

3.4.2 Membranes preparation ................................................................. 40
3.5 References ......................................................................................... 41

4. Asymmetric membranes ........................................................................ 43
   4.1 Introduction ......................................................................................... 43
   4.2 Membranes preparation ...................................................................... 47
   4.3 Conclusions ......................................................................................... 61
   4.4 Experimental part .............................................................................. 62
      4.4.1 Particle synthesis and coating ....................................................... 62
      4.4.2 Synthesis of asymmetric membranes ........................................... 65
   Appendix .................................................................................................. 67
   4.5 References ......................................................................................... 71

5. Porous membranes with functionalized pores – silica rings ............... 73
   5.1 Introduction ......................................................................................... 73
   5.2 Pore functionalization and silica ring preparation ......................... 75
   5.3 Conclusions ......................................................................................... 81
   5.4 Experimental part .............................................................................. 82
   5.5 References ......................................................................................... 84

6. Mixed matrix membranes for gas separation ....................................... 87
   6.1 Introduction ......................................................................................... 87
   6.2 Theoretical description of gas transport in mixed matrix membranes ........ 88
   6.3 Membrane preparation ..................................................................... 99
   6.4 Conclusions ......................................................................................... 109
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>Experimental part</td>
<td>110</td>
</tr>
<tr>
<td>6.5.1</td>
<td>Preparation of carbon molecular sieves</td>
<td>110</td>
</tr>
<tr>
<td>6.5.2</td>
<td>Preparation of mixed matrix membranes on the Langmuir trough</td>
<td>112</td>
</tr>
<tr>
<td>6.6</td>
<td>References</td>
<td>114</td>
</tr>
<tr>
<td>7</td>
<td>Conclusions</td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>Acknowledgments</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Curriculum Vitae</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>Selbständigkeitserklärung</td>
<td>124</td>
</tr>
</tbody>
</table>
# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
<td>APT</td>
<td>3-Aminopropyltriethoxysilane</td>
</tr>
<tr>
<td>CaF₂</td>
<td>Calcium fluoride</td>
</tr>
<tr>
<td>Eqn.</td>
<td>Equation</td>
</tr>
<tr>
<td>Fig.</td>
<td>Figure</td>
</tr>
<tr>
<td>H</td>
<td>Thickness of the oil layer</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>HEMATMDI</td>
<td>Dimethacrylate 11,14-Dioxa-2,9-diazaheptadec-16enoic acid,4,4,6,16-tetramethyl-10,15-dioxo,-2-[(2-methyl-1-oxo-2-propen-1-l)oxy]ethylester</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric acid</td>
</tr>
<tr>
<td>HRSEM</td>
<td>High Resolution Scanning Electron Microscopy</td>
</tr>
<tr>
<td>KF</td>
<td>Potassium fluoride</td>
</tr>
<tr>
<td>lim</td>
<td>Limes</td>
</tr>
<tr>
<td>NaF</td>
<td>Sodium fluoride</td>
</tr>
<tr>
<td>ODES</td>
<td>n-Octadecyltriethoxysilane</td>
</tr>
<tr>
<td>( P_{\text{Brügemann}} )</td>
<td>Membrane permeability described by Brügemann model</td>
</tr>
<tr>
<td>( P_c )</td>
<td>Permeability of continuous phase</td>
</tr>
<tr>
<td>( P_d )</td>
<td>Permeability of dispersed phase</td>
</tr>
<tr>
<td>PFOTE</td>
<td>1H,1H,2H,2H-Perfluoroctyltriethoxysilane</td>
</tr>
<tr>
<td>( P_{\text{Maxwell}} )</td>
<td>Membrane permeability described by Maxwell model</td>
</tr>
<tr>
<td>( P_{\parallel} )</td>
<td>Membrane permeability described by parallel model</td>
</tr>
<tr>
<td>( P_{\text{serial}} )</td>
<td>Membrane permeability described by serial model</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>R</td>
<td>Particle radius</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>Si-APT</td>
<td>Silica particles coated with 3-Aminopropyltriethoxysilane</td>
</tr>
<tr>
<td>Si-PFOTE</td>
<td>Silica particles coated with 1H,1H,2H,2H-perfluoroctyltriethoxysilane</td>
</tr>
<tr>
<td>Si-TPM</td>
<td>Silica particles coated with [3-(Methacryloxy)propyl]trimethoxysilane</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethylorthosilicate</td>
</tr>
<tr>
<td>TPM</td>
<td>[3-(Methacryloyloxy)propyl]trimethoxysilane</td>
</tr>
<tr>
<td>TMPTMA</td>
<td>Trimethylolpropane trimethacrylate</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet light</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
</tr>
<tr>
<td>V_o</td>
<td>Volume of oil</td>
</tr>
<tr>
<td>V_p</td>
<td>Volume of particles</td>
</tr>
<tr>
<td>α</td>
<td>Ratio of permeabilities of dispersed phase to continuous phase</td>
</tr>
<tr>
<td>φ</td>
<td>Volume fraction</td>
</tr>
<tr>
<td>φ_c</td>
<td>Volume fraction of continuous phase</td>
</tr>
<tr>
<td>φ_d</td>
<td>Volume fraction of dispersed phase</td>
</tr>
<tr>
<td>θ</td>
<td>Contact angle</td>
</tr>
<tr>
<td>θ_{a/o/p}</td>
<td>Contact angle at the air/oil/particles interface</td>
</tr>
<tr>
<td>θ_{w/o/p}</td>
<td>Contact angle at water/oil/particle interface</td>
</tr>
<tr>
<td>ρ_p</td>
<td>Density of particle</td>
</tr>
<tr>
<td>ρ_o</td>
<td>Density of oil</td>
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"Membrane Science", the separation of components out of mixtures by passing them through a thin sheet of selective permeability is comparatively young. First observations of typical membrane properties were for example reported by Abbè Nolleti in 1748 who filled a pig bladder with “spirit of wine” immersed it into water and observed a pressure rise and finally bursting of the bladder [1] – an observation which we nowadays call osmotic effect caused by a selectivity of the bladder for water. Selective transport again was responsible for a curious observation made by Doebereiner in 1823, who reported that hydrogen (but not air) encased in a glass jar with tiny cracks would not only escape but even create a reduced pressure. In 1833 Thomas Graham inspired from Doebereiner’s experiment made quantitative measurements of hydrogen permeability, replacing the ‘crack’ in the glass jar systematically by thin sheets of various materials and characterizing their permeability [2], he as well studied permeabilities of dissolved and dispersed matter through membranes and used permeability through a membrane as a criterion to distinguish between solutions and dispersions [3]. It still took until the 20th century until the first synthetic membranes were made by a company: in 1920 first synthetic membranes from cellulose nitrate or cellulose nitrate-cellulose acetate were prepared by the German Company Sartorius Werke GmbH. They were used as a bacteria filter but only on the laboratory scale [4], since then there has been significant improvement in performance or durability and hence a continuously rising market for membranes developed.
Chapter 1  General introduction and outline of this thesis

The key property of a membrane is selective transport: a desired component out of a mixture is either retained or passes preferentially through it. The membrane might be selective based on chemical differences like polarity, volatility, charge or might select components just by their size. These selectivities might be used to separate gas mixtures like oxygen/nitrogen, methane/carbon dioxide or methane/butane, liquid mixtures like aromatic hydrocarbons/aliphatic hydrocarbons, ethanol/water or solutions like salt/water or to separate particles out of dispersions. In general the membrane might be homogeneous or dense, selectivity being a result of differences in solubility or diffusion coefficient, or it may contain pores, selectivity in this case being based on the size of the permeating substances.

Gas separation is a field in which membranes are widely used. One of the examples of application of industrial membranes is enhanced oil recovery. In this process carbon dioxide is injected into the well to dissolve oil and to lower its viscosity. When oil is then pumped to the surface, carbon dioxide is removed by gas separation membranes from the mixture of hydrocarbons and the significant amount of methane. The natural gas is then used as fuel and carbon dioxide is reinjected into the well. Another field of membrane application is removal of carbon dioxide from methane that is obtained from natural gas wells [5], biogas or gas recovered from landfills. Natural gas contains various amounts of carbon dioxide depending on the source, while gases that stem from anaerobic decomposition of organic matter e.g. biogas recovered from a landfill sites contain [6, 7] 54 – 59 % mol of methane and 40 – 45 % mol of carbon dioxide. This carbon dioxide reduces the heat of combustion per norm volume and causes corrosion problems. The majority of the carbon dioxide is removed using membranes; the final gas purification is obtained by an amine absorption process.

Ultrafiltration and reverse osmosis become very attractive in a lot of applications, for example: paint solvent recovery [8], treatment of used lubricating oil, edible oil processing.

Solutions of automated painting baths consist of solvents, resins and pigments [9]. When the bath needs to be exchanged (e.g. because the color of the production line is varied) at least part of it needs to be treated as waste. Ultrafiltration or reverse osmosis membranes are used to separate solvents from the remaining part of solution. Thus, the solvent is recovered and can be reused for the preparation of new painting bath solutions.

Lubricating oils become contaminated by combustion byproducts like polymers, asphaltenes or attrition. These impurities can be removed via ultrafiltration processes and the oil is further used.
During edible oils preparation [9], often raw materials are extracted with different solvents like: ethanol, isopropanol or hexane. After extraction, solvents are separated from the oils via distillation or by ultrafiltration or reverse osmosis processes.

Nowadays there are several methods used for synthetic membranes preparation [10]. Continuous or dense membranes usually are made by coating: a thin layer of a melt or solution is applied to a solid substrate, solidified and afterwards separated from it again. Less often used is melt spinning or melt blowing: a melt of suitable viscosity (usually an organic polymer) is pressed through a thin slit and subsequently thinned down by stretching or blowing.

More elaborate is the preparation of porous membranes. The most important techniques are: sintering, stretching, track etching and phase inversion.

During sintering, grains of material (inorganic or organic) with defined diameter are compressed together and sintered or glued together in such a way that there is still a continuous phase in between them. Organic as well as inorganic materials or mixture of both are used for the membranes preparation with this method. Free spaces that are obtained between particles define the pores diameter. Thus, the particles size distribution has a decisive influence on the pore sizes in the membrane. The narrower the particle size distribution, the more homogenous pores sizes are obtained. The most often used materials that are processed with this method are: polyethylene, polypropylene, stainless steel and ceramic.

Another method used for the membrane preparation is stretching of semi crystalline polymers. Semi crystalline polymers are extruded to thin foils in such a way that crystallites are oriented preferentially parallel to the extrusion direction. By applying a force perpendicular to them, the remaining amorphous part of the polymeric matrix brakes down into thin fibrils. In between these fibrils, slit-like pores in the range from 0.1 µm to 3 µm are obtained [10].

Cylindrical pores are obtained during track etching. Polymeric foils are bombarded with high energy particles and this creates linear paths of destruction in the polymeric matrix. Then the foil is immersed in the bath with alkaline solution where polymer is etched along these paths and finally membranes with cylindrical pores are obtained, the pore width being tailored by the etching time.

Phase inversion method is a technique in which polymeric materials are transferred from liquid to solid state. The above mentioned early membranes, prepared by Sartorius Werke GmbH for example were prepared using a phase inversion method that was introduced by Zsigmondy. In the earliest method polymeric membranes were prepared in such way that dissolved polymer was
cast onto the solid substrate and then it was placed in the vapors of nonsolvent saturated with solvent. Due to the high concentration of solvent above the polymeric layer, solvent didn’t evaporate from the cast film. Solidification of the membranes was caused by diffusion of nonsolvent into the film. This finally leads to the porous membrane formation. In the next technique, a stable polymeric solution that consists of solvent and nonsolvent is cast onto the solid support and then the solvent evaporates from the film. In this case solvent is more volatile then nonsolvent and due to faster evaporation of the solvent, the polymer starts to precipitate and a porous membrane is obtained. Another technique is thermal precipitation where a cast polymeric solution that consists of one or several solvents is cooled down till phase separation occurs. Immersion precipitation is next method for the membranes preparation and nowadays most of the commercially available membranes are made with this technique. During this process a layer of a stable polymeric solution, which contains solvent and nonsolvent is immersed into a nonsolvent bath. Depending on the ratios of solvent to nonsolvent as well as the solvent volatility various membranes morphologies can be obtained.

Another method for the preparation of porous materials which can be used for the generation of porous membranes is the embedding of sacrificial particles into a solid matrix. Removal of these particles finally gives rise to a porous material. [11-17] E.g. a mixture of particles and a polymerizable liquid has been enclosed between two planar substrates, the liquid was solidified by polymerization and the particles were removed [18].

One special type of membranes is so called ‘asymmetric membranes’. Often materials with a desirable selectivity have only a low permeability. Thus, in order to achieve reasonably low permeation resistance, these membranes need to be made as thin as possible. This, however, reduces their mechanical stability. The common solution is to back-up these membranes by a suitable porous structure. However, if this supportive structure needs to be added after membrane preparation, the mechanically unstable membranes still need to be handled in some intermediate stages. Thus, there have been various strategies developed which generate such a desired structure in one stroke. The most elegant method to achieve this has been realized in suitably conducted precipitation processes. If done correctly, the above mentioned phase separation processes might yield a top layer that is non porous or has fine pores and is supported by a layer comprising large pores or a layer comprising pores whose diameter increases with increasing distance to the top surface.
Membranes that will be shown along this thesis are membranes based on the removal of embedded sacrificial particles but prepared on the basis of a special phenomenon called “particle assisted wetting”. It was observed that mixtures of hydrophobized silica particles with an oil form wetting layer on the water surface in such way that particles adhere to the air/oil and water/oil interface [19]. Interesting is that the same oil would not wet a water surface but will create lenses (Figure 1).

![Diagram of particle assisted wetting method]

Figure 1: Principle of particle assisted wetting method.

Partial replacement of the water/oil interface by solid particles causes reduction of the total interfacial energy at the fluid/fluid interface and this gives rise to the hybrid monolayer [19].

It was shown that the phenomenon of particle assisted wetting can be used as tool for porous membranes preparation [20-22]. Schematic procedure of porous membrane preparation is shown in Figure 2. First a mixture of hydrophobized silica particles with monomer, solvent and photoinitiator is applied onto the water surface. After solvent evaporation particles penetrate the oil layer and adhere to the air/oil and to the water/oil interface. The monomer then is solidified with UV light and the resulting composite membrane is transferred to solid support. Then particles are etched from the polymeric matrix with hydrofluoric acid from the gas phase and this gives rise to the porous membrane.
In Figure 3 are shown SEM images of porous membranes prepared with the particle assisted wetting method. Pore diameters depend on the particle sizes and membranes with pores in the range from 50 nm to 1 µm have been prepared. Another important issue is that the membrane thickness is in the range of 70 – 80 % of particles diameter (Figure 3a), therefore freely suspended membranes with these thicknesses are too fragile to use them in the pressure filtration. In Figure 3a can be seen that pores are concave and on the pores walls are small “windows” visible which indicate that particles touched each other.

Figure 2: Procedure of porous membrane preparation.
Chapter 1  General introduction and outline of this thesis

On Figure 3b is shown a porous membrane that is transferred onto the TEM grid with an area of around 30 mm$^2$.

In the chapter 2, strategies of membrane preparation that will cover areas exceeding by far the previous limitation of 30 mm$^2$ will be shown. Membranes will be supported not only on a tiny TEM grid but on non-woven fibrous support. It will be shown that polymeric matrix will be bond to fleece fibers.

It had been shown that membranes with pore diameters up to 1 µm can be prepared [21]. In the chapter 3 it will be shown that pores with 75 µm in diameter can be achieved, using glass beads as porogens for the membranes preparation.

Porous membranes with pore widths smaller than 100 nm are very fragile and quite often they were damaged during transferring onto the support. To improve membranes stability with pore diameters of 100 nm and below, asymmetric membranes will be prepared. In chapter 4 it will be shown that when a mixture of two sorts of particles with opposite surface properties is applied with oil to the water surface then a composite layer is obtained. In this layer more hydro-

Figure 3: Porous membranes prepared with particle assisted wetting method [20, 21]
phobic particles adhere to the air/oil and less hydrophobic particles to the water/oil interface respectively [22]. After solidification of the oil and removal of the particles, porous asymmetric membrane is obtained with pores that are created at the contact places between particles which adhere to the different interfaces.

Etching of particles from the composite monolayer was made in the vapors of hydrofluoric acid when the membrane was transferred onto a solid support. In chapter 5 a new concept of pore functionalization will be shown. Partial etching of silica particles on the water surface instead of on solid support gives rise to the rings that remained inside pores.

In the 6th chapter instead of impermeable silica particles highly permeable and selective carbon molecular sieves are embedded in the polymeric matrix. Theoretical predictions of gas transport through composite membranes, where particles protrude at the top and the bottom from the polymeric matrix, show that this membrane architecture has major influence on the permeability and selectivity through the membrane.

In the last chapter all results presented in this work will be summarized and conclusion will be drawn.
1.1. References


Chapter 2

Porous membranes on supportive structure

2.1. Introduction

Microsieves are membranes that have uniform pore sizes, sharp pore sizes distribution, a thickness is in the range of the pore size diameter and thus allow a high flux through the membrane [1-5]. The low thickness, however, means as well that microsieves can be destroyed during filtration by the pressure applied to its surface. Thus, microsieves very often need to be supported by a porous support which will give them higher mechanical stability. There are several approaches that are used to improved mechanical stability of microsieves.

One of the applied concepts to create supported microsieves is photolithography. In this approach a silicon wafer is used as supportive structure [6]. On top of that substrate, silicon nitrate is deposited. Then the deposited layer is structured via photolithography and finally the remaining part of the substrate is removed via anisotropic etching [7]. With this method regular pore patterns with constant distance in between the pores are obtained. Usually the pore spacing is two times bigger than the pore diameters.

Another concept which is used to attach a membrane to supportive structures is heterogeneous graft polymerization [8-12]. This method gives rise to in suit layer formation on top of the support and at the same time to the attachment of new created polymeric layer to the support. A photoinitiator is dissolved in a solvent which is not soluble or even would not cause swelling of a support [8]. After solvent evaporation a monomer saturated with photoinitiator is applied on top
of the support and then polymerization is induced by UV light. During polymerization the monomer is added from the gas phase.

This technique was used to modify the ultrafiltration polyacrylonitrile membranes [11]. The modified membranes were used for proteins separation. These membranes are prepared in such way, that first solution of benzophenone in methanol is applied onto top of polyacrylonitrile layer. After methanol evaporation the monomer – acrylic acid – is added from the gas phase and then is polymerized with UV light. Because of the limited volatility of many attractive monomers, this method had been extended to the UV initiated grafting polymerization from the aqueous monomer solutions.

Another way of membrane deposition onto supportive structures is the Langmuir-Blodgett technique. In this method monolayers of macromolecules (e.g. cellulose ethers functionalized with isopentyl cinnamyl) are transferred onto a porous polypropylene membrane (e.g. Celgard 2400). Functionalized groups that are attached to the cellulose ethers allow photocrosslinking after transfer. After deposition of 48 - 70 layers, membrane is cross-linked with UV light [13].

As already mentioned in the first chapter of this thesis, spreading of hydrophobized silica particles with oil, photoinitiation and solvent onto the water surface give rise to composite layer where particles protrude at the top and at the bottom. Then solvent is evaporated and composite layer is solidified with UV light. Next the particles are etched with vapours of hydrofluoric acid. Removal of the particles gives rise to porous membranes with uniform pore diameters in the range of 70% - 80% of the particle diameters [14-15]. Porous membranes that are obtained with this technique usually are too fragile to operate them in pressure filtration processes.

Thus, the idea pursued in this chapter is to bond the microsieves obtained with particle assisted wetting method with cheap support like non woven fibrous support (Figure 1).

![Figure 1: Desired membrane structure bonded to the fibrous support.](image)
2.2. Membrane preparation

To obtain the desired membrane structure that is attached to a fleece two procedures are used. First approach that is used to bond porous membrane with non woven fibrous support is shown in Figure 2.

Figure 2: Preparation of the porous membrane by subsequent deposition onto the support.
A fleece is placed at the bottom of the water filled Petri dish. Then the mixture of silica particles, oil, photoinitiator and solvent is applied onto the water surface above the immersed fleece. Next the water level is lowered to such an extend that composite layer that is floating on the water surface touches fibres that are protruding out from the water. Then solvent is evaporated and the oil is cross-liked with UV light. After membrane solidification, fleece and composite membrane are transferred into the Petri dish and dried in the air at room temperature. After drying, membrane and support are cut into smaller pieces and then exposed to vapours of hydrofluoric acid to remove silica particles. Pristine fleece, composite membrane on the fleece and porous membrane after removal of particles are imaged with scanning electron microscopy.

Overview and SEM pictures of the pristine fleece are shown in Figure 3.

![Figure 3: Overview and scanning electron microscopy images of the pristine fleece.](image)

As can be seen in Figure 3 the fleece consists of fibres with approximately 20 µm in diameter. In Figure 4 are shown images of composite membrane attached to the fleece.
Chapter 2  Porous membranes on supportive structure

Figure 4: Composite membrane attached to the fleece.
In Figure 4a it can be seen that quite a big area of the fleece is covered with a composite membrane with embedded silica particles. The membrane is attached to separate fibres but it is not flat and uniform. The biggest parts of the composite membrane are bonded with fibres but between them it is broken. The cracks in the composite membrane are obtained when membranes and fleece were cut into smaller fragments. During cutting, fibres were bended and membranes that were bonded with them are too rigid to stand that tension. Another important issue is that there is good connection between fibres and layer of particles and polymer (Figure 4b - d). Most of fibres are completely covered with the composite layer.

In Figure 5 are shown pictures of membranes after etching of silica particles.
Figure 6: Porous membrane attached to the fleece.
After etching of particles, the area of the fleece that is covered by the membrane is smaller than before etching. Porous membrane is visible only between fibres that are in the comparatively small distance from each other (Figure 6a) other parts of the fleece are non covered. It is suspected that during transferring of the membrane bending of fibres cause destruction of the polymeric layer. In Figure 6b – d it can bee seen that the surface of separate fibres is covered with porous members, this indicates that the membrane was attached to the substrate but then was destroyed by fibres bending. To find out how big an influence the bending of fibres has on the membrane stability, the procedure of membrane preparation is changed. This new way of membrane preparation is shown in Figure 7.

![Diagram showing membrane preparation process](image)

**Figure 7: Membranes with 500 nm in diameter silica particles.**
In this case the fleece is cut into pieces of the desired size before composite layer deposition. These pieces of fleece are glued to the carbon tape that is used as support for the scanning electron microscopy measurements and then won’t be cut or bend anymore. This is the decisive difference to the previous procedure where fleece was first cut after photopolymerization into the smaller fragments. Then the carbon support with fleece on top of it is immersed into ethanol and then into water. When the fleece is completely wetted, mixture of silica particles, oil, photoinitiator and solvents are spread on top of the wetted fleece. After solvent evaporation the oil is cross-linked with UV light. After membrane solidification, water which wetted the fleece is exchanged with ethanol. Then the fleece with attached composite membrane on top of it is dried in the air and at room temperature. Afterwards silica particles are removed from the composite membrane with vapours of hydrofluoric acid. As in the previous procedure composite membrane before and after removal of particles are imaged with scanning electron microscopy. In Figure 8 are shown images of composite membranes attached to the fleece.

In Figures 8a - b can be seen that the membrane surfaces have not as many brakes as before. The membrane is homogenous and only at the rim of the fleece cracks are visible. Some of the fibres protrude from the composite layer (Figure 8b). In Figure 8c can be seen that fibres that protrude from the fleece are bond with membrane. As in the previous procedure, the membrane that is attached to the fleece is not flat. Fibres that are bend and only slightly protrude from the fabric shape the membrane surface. On the water surface that creates capillary bridges between fibres, particles and oil assemble as composite layers which after solidification have the same shape as the water bridges. In Figure 9 are shown photos of porous membranes attached to the fleece.
Figure 8: Composite membrane attached to the fleece.
On the overview picture it can be seen that there are no new cracks visible (Figure 9 a). The fibres that are bond with the polymeric layer are well visible and the membrane surface shape is...
structured by fibres that are bend but their ends do not protrude out to the air. On the image with higher magnification (Figure 9b, c) bigger holes with diameters in micrometer range are visible. Due to the fact that in the membranes before etching no holes with similar diameter are visible it is assumed that these openings are created during etching. One explanation for this phenomenon can be that particles that were spread onto the wetted fleece create agglomerates and finally they template bigger holes in the polymeric matrix.

Second procedure of porous membrane preparation on the fleece gives better results. Fleece immobilization on the carbon grid causes that on the membrane surfaces there are not so many cracks visible and bigger area of the fabric is covered with homogenous porous membrane. Spreading of the mixture of particles and oil directly onto wetted support gives rise to the more homogenous membrane, but there is still one important issue that is similar for both procedures – the surface of the membrane is not flat. This corrugated surface of the membranes will cause a lot of problems during cross flow filtration. In membranes “valleys” particles could not be washed and finally they will clog the pores.
2.3. Conclusions

Two procedure of membranes deposition onto the non woven fibrous support were shown. The first procedure, where particles and oil are spread onto the water surface and then are transferred onto the fleece gives rise to the membranes with a lot of cracks in the polymeric layer. The second method, where particles and oil are directly spread onto the wetted fleece gives rise to the almost crack free membranes that cover a much bigger area of the fabric.

Membrane surfaces obtained with both methods are not flat. Corrugation of membrane surface is one of the most important issues for microsieves that are used for cross flow filtration. In “valleys” of membranes with corrugated surfaces particles will settle down and they will clog the pores. Finally this will cause smaller efficiency of the filtration process. For that reason microsieves prepared with the particle assisted wetting method need to be supported on some flat support. The preparation of the flat support for membranes with pores diameter in submicroscopic range will be shown in the chapter 3 of this thesis.
2.4. Experimental part.

2.4.1. Particle preparation.

Particles are synthesized in a Stöber [16] type synthesis and subsequently coated in a one pot procedure [17].

At the beginning of the synthesis, 8 ml of TEOS (tetraethyl orthosilicate, Sigma Aldrich 98%), 25 ml of ammonia (25% by weight, technical grade) and 1 ml of water are added to 200 ml of ethanol (98 %, technical grade) in a 500 ml round bottom flask at constant stirring rate and at room temperature. After four hours again 1 ml of TEOS, 2 ml of ammonia, 1 ml of water are poured into the reaction medium. Finally after another hour, 0.5 ml TPM [3-(methacryloyloxy)propyl] trimethoxysilane (Sigma Aldrich, 98 %) is added. After 5.5 hours, ammonia is evaporated at reduced pressure with a water jet aspirator pump, then water and ethanol are removed with a rotary evaporator at reduced pressure generated by a rotary pump. The crude white powder is subsequently washed with ethanol with five cycles of centrifugation with speed of 6000 rpm. After the washing process, a dispersion of a mass fraction of 20 % of particles in ethanol is prepared.

Particle sizes and shapes are characterized with scanning electron microscopy (NanoNovaSEM, Company FEI). A droplet of the dispersion of particles in ethanol 0.05 % (weight fraction) is deposited onto a silicon wafer and imaged with SEM. Particles are 474 nm in diameter and the standard deviation is 16 nm. (This analysis is based on 80 particles). Given the obtained standard deviations, rounded values (470 nm) are used throughout the descriptive parts of this chapter.

Figure 10: Silica particles, 470 nm in diameter.
2.4.2. Preparation of membranes attached to the fleece via decreasing of the water level.

A round piece of fleece with 5 cm in diameter is completely immersed into a water-filled Petri dish (5.5 cm in diameter). Then the mixture of silica particles with trimethylolpropane trimethacrylate, benzoinisobuthylether, ethanol, chloroform is applied onto the water surface. The amount of spreading solution was chosen in such a way that the silica particles if completely spread would yield a close-packed monolayer on the entire surface available. Exact composition of the mixture is given in the table 1. Then the solvent is evaporated over 15 minutes. Then the water is removed with a syringe to such a level that the composite monolayer from particles and monomer touched the immersed fleece. Afterwards the monomer is cross-linked by irradiation with UV-light of 250 nm wavelength (low pressure mercury lamp UMEX Dresden with emission predominantly of 250 nm wave length, intensity $0.0798 \text{ W/cm}^2$). (Caution! Ultraviolet radiation of this wavelength and intensity is dangerous to the eyes, it may be used only in closed compartments that exclude the possibility of stray light reaching unprotected eyes.)

After solidification of the polymer, the fleece with the membrane attached to its surface is dried in room temperature over 12 hours. This dried fleece is then cut into smaller parts. Next, dried membranes are placed into the plastic Petri dish and exposed for 15 minutes to the vapours of hydrofluoric acid (40%) (Fluka) (Caution! Hydrofluoric acid is toxic and corrosive and should be handled only by trained personnel aware of the dangers associated with the use of this chemical!). Membranes before etching and after removal of particles are characterized with Scanning Electron Microscopy.

Table 1: Composition of the spreading solution used for the preparation of membranes via lowering the water level.

<table>
<thead>
<tr>
<th>Components</th>
<th>Mass [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica particles in ethanol 20% (weight)</td>
<td>0.016</td>
</tr>
<tr>
<td>3 % (by weight) TMPTMA in ethanol : chloroform (1:1 by volume)</td>
<td>0.0245</td>
</tr>
<tr>
<td>Benzoinisobuthylether</td>
<td>0.0002</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.327</td>
</tr>
</tbody>
</table>
2.4.3. Preparation of membranes on the wetted fleece.

A round piece of fleece with 5 cm in diameter is completely drained with ethanol and then immersed into the purified water. Then, the mixture of silica particles with trimethylolpropane trimethacrylate, photoinitiator – Lucirin TPOL (BASF), ethanol, chloroform is applied onto the water surface of the drained fleece. Exact composition of the deposited mixture is given in the table 2. The amount of spreading solution was chosen in such a way that the silica particles if completely spread would yield a close-packed monolayer on the entire surface available. Next, the solvent is evaporated over 40 minutes. Afterwards, the monomer is cross-linked by irradiation with UV-light of 360 nm wavelength (Lamp Benda, Company Laborgeräte und Ultraviolettstrahler, Wiesloch). After solidification of the polymer, water from the fleece is extracted with ethanol, and left 12 hours. Dried fleece is then cut into smaller parts. Next, dried membranes are placed into the plastic Petri dish and exposed for 15 minutes to the vapours of hydrofluoric acid (40%) (Caution! Hydrofluoric acid is toxic and corrosive and should be handled only by trained personnel aware of the dangers associated with the use of this chemical!). Membranes before etching and after removal of particles are characterized with Scanning Electron Microscopy.

Table 2: Composition of the spreading solution used for the preparation of membranes via deposition on top of a wetted fleece

<table>
<thead>
<tr>
<th>Components</th>
<th>Mass [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica particles in ethanol 20% (weight)</td>
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</tr>
<tr>
<td>3 % (by weight) TMPTMA in ethanol : chloroform (1:1 by volume)</td>
<td>0.0466</td>
</tr>
<tr>
<td>Lucirin TPOL (BASF)</td>
<td>0.001</td>
</tr>
<tr>
<td>Ethanol/chloroform mixture (1:4 by weight)</td>
<td>0.3878</td>
</tr>
</tbody>
</table>
Chapter 2  Porous membranes on supportive structure

2.5. References

Chapter 3

Porous membranes with pores in micrometer range

3.1. Introduction

Microsieves - porous membranes with uniform pore size, a thickness in the range of the pore size and high porosity - are important materials for advanced filtration applications [1]. The main advantages of these structures are: sharp size selectivity and high flux that can be obtained during filtration [2-4]. Microsieves originally were prepared in pioneering work by C. van Rijn using photolithography [5-11]. C. van Rijn further developed variations in which randomly placed particles are used as porogenes and in which polymeric microsieves are cast using a master that was made by photolithography [12-15]. In our group a method was developed to cast microsieves on a water surface using mixtures of sacrificial particles that act as porogenes and non volatile organic 'oils' that were polymerized [16-17].

During operation of microsieves in filtration – as in most filtration applications as well - often fast cake layer formation occurs. The microsieves, however offer the unique advantage that their surface is flat, that there are not tortuous paths within the interior and that all particles that are retained at the upper interface. Due to this feature, the cake can efficiently be removed using a combination of cross-flow filtration with back flushing [1, 3-4 14]. Microsieves used for this kind of filtration need to have a flat surface to make the removal of the particles from the surface easier. Another important issue is an as small as possible distance between pores so called “pitch”
sizes. When the pitches are smaller than the particles diameter, the possibility of the cake layer formation is lower [3, 15].

The low thickness of microsieves is of advantage – it reduces the flow resistance and the probability of particle trapping – but at the same time it renders the mechanical fragility, especially if the pore sizes and thus the thickness is below one micrometer [3]. In filtration applications it is usual to integrate delicate membranes into a hierarchical supportive structure or mount them on top of it. This strategy has already nicely been applied by C. van Rijn in his microsieves made by photolithography. In photolithography it is straightforward to integrate a hierarchical structure; this needs additional process steps, but is done with the same setup.

In this approach of casting microsieves onto a water surface, however, such hierarchical structures are missing and it seems not straightforward to integrate them into the process.

However, in our case it is comparatively easy to vary the pores sizes of the membranes, just by using appropriate particles. Thus, one strategy to achieve hierarchical structures may be to prepare a set of membranes of varying pore sizes and mount them together into a hierarchical structure. For example, hierarchically structured membranes that consist of few membranes that are lie on top of each other like the one schematically shown in Figure 1:

![Figure 1: Hierarchically structured microsieves made by mounting several microsieves into a stack.](image)

In principle, one might use as supportive structures with larger pores commercially available materials like woven or non woven fibrous materials or sponge-like membranes obtained via phase separation processes. However usually these supports have irregularly redistributed pores, are not sufficiently flat and are too thick. In principle one might prepare the coarse supportive structure using our technique of ‘particle assisted wetting’. However, until now the maximum size of particles that were used was 1 µm.
Thus, the idea pursued here is to prepare porous membranes with pores in more than micrometer size range with regularly redistributed and dense packed pores. To obtain such porous membranes, suitable particles need to be made or obtained commercially, spread with oil onto the water surface in such a way that they are embedded preferentially in the centre of the oil layer, and after solidification of the oil they need to be removed. Given the experience with silica beads that already existed in our group this seems to be straightforward, however, some restrictions need to be taken into account:

(i) There are no silica beads in the desired size range commercially available nor does the particle synthesis according to the original Stöber process [18] allow exceeding 1µm diameter. There are a few papers describing the synthesis of 'large' silica beads by extensions of the Stöber process [19-21], but even these papers do not exceed diameters of 2 µm.

(ii) If beads other than silica are chosen, one needs to control the contact angles of the oil at the water/oil/particle as well as the air/oil/particle interfaces and has to think up ways of selectively removing the particles out of the cross-linked membrane.

(iii) In the case of submicrometric particles it was safe to neglect gravity; in case of larger particles gravity for sure can not be neglected and thus somehow needs to be counterbalanced.

Taking all these considerations into account, glass beads were chosen as sacrificial particles. These glass beads are commercially available with pretty narrow size distribution, being similar to silica they can be modified with the same silanization agents we already gathered experience when working with silica particles and may in principle as well be removed via etching with hydrofluoric acid. However, in all steps of the process conducted with glass beads the side constraints need to be taken into account.

Before silanization, the glass surface needs to be activated. When etching the glass beads with hydrofluoric acid, non volatile and even non soluble by-products are formed (NaF, KF, CaF₂), thus the previously practised dry etching through the gaseous phase can not be followed, but might be replaced by suitable wet etching processes. Finally then the more significant role of gravity leads to the expectation that the big particles will penetrate more deep into the liquid phases of lower density than was observed in the case of submicrometric particles. This might be counteracted by choosing other surface properties than those that were optimal in the case of small particles. In the following, the corresponding experiments and steps of optimization will be detailed. A sketch of the finally successful procedure is already given in Figure 2.
Chapter 3  Porous membranes with pores in micrometer range

Figure 2: Preparation of a porous membrane with pores in micrometer range, a) water surface, b) spreading of glass beads, c) dense monolayer of particles on the water surface, d) addition of oil, e) solvent evaporation, f) composite monolayer on the water surface, g) photo cross-linking of the oil, h) solidified composite layer on the water surface, i) etching on the mixture of hydrofluoric and sulphuric acids, j) porous membrane
3.2. Membrane preparation

As described in [16, 17] the spreading of an oil and suitable particles on the water surface yields a composite layer. In this layer, spherical colloids protrude out at the top and at the bottom from the oil. For the performance of the final microsieve, the particles should finally be positioned in the centre of the polymeric layer. This position in the polymeric layer depends on the contact angles at the air/oil/particles and at the water/oil/particles interfaces. After solidification of the oil and removal of the particles, the porous membrane is created. The goal of this chapter is to create microsieves with hole sizes well above one micrometer. In order to achieve this glass beads were chosen. These are commercially available in the desired diameter of 75 µm and with a narrow size distribution (Supelco).

In case of submicrometric particles, the contact angles were already varied in a non-systematic manner by application of several surface functionalizations by Hui Xu [22]. A thorough systematic investigation comprising 12 silanization agents and the quantitative determination of contact angles at the air/oil/particles and at the water/oil/particles interfaces were made by Ailin Ding [23]. In those experiments the coating agents were organically modified triethoxysilanes that differ from each other by the organic group attached to them. The resulting coatings changed the properties of the particles from hydrophilic to the very hydrophobic. The result of these investigations can be summarized as such, the optimum coating, that gives the submicrometric particles similar affinity to the upper and the lower interface are those of intermediate hydrophobicity, such as ester groups. As a consequence the commonly used surface coating for submicrometric particles in the work of Hui Xu and Feng Yan was bearing methacrylate groups. Particles with more hydrophilic coatings, such as amino groups had a tendency to protrude too much out of the lower interface; those with completely hydrophobic coatings such as fluorinated organic chains had a tendency to protrude predominantly out of the upper interface.

In case of submicrometric particles, gravity can be neglected, but if the applied particles have diameter bigger than 1 µm – as those used here - the gravity in all likelihood will push them further down into the subphase and surface properties need to be optimized again. Thus, it was chosen to modify the much bigger and heavier particles used here again with various silanization agents and check the position of the embedded particles as a function of the surface coating.

The surfaces of the glass beads with 75 µm in diameter to be used for the membrane preparation are modified with three different silanes of increasing hydrophobicity: aminetrieth-
oxy silane (APT), trimethacryloxypropyl triethoxy silane (TPM), n-octadecyl triethoxy silane (ODES). It turned out that the reproducibility of the surface treatment is insufficient, if the beads as received are silanized. In order to achieve reproducible results, the beads needed to be cleaned or 'activated' by treatment with a mixture of hydrogen peroxide and sulphuric acid. Beads pre-treated by such a procedure are coated in a reproducible manner.

Initial experiments for the preparation of membranes using these large beads were done following the original procedures developed for submicroscopic beads. These procedures comprise the preparation of a dispersion of the beads in a volatile spreading liquid, that comprises as well the non volatile 'oil' and the spreading of this dispersion onto the water surface. However, this procedure was impractical. The bigger beads sedimented fast, in the storage container, as well as in the syringe, had a tendency to cling to the walls of the container and to clog the needle, if a syringe was used for the spreading. Thus an alternative method for applying the particles had to be developed. Finally successful was to apply the particles as dry powder to the water surface of a Petri dish that was half-filled with water. Fortunately in dry substance such big particles have minimum tendency to aggregate, this is in strong contrast to the behaviour of the submicroscopic particles, which have a high tendency to cluster in dry form. Thus it was feasible to apply the particles as a first step of membrane preparation as dry powder to the water surface and wait for them to spread out as a monolayer. At the beginning, surface modified glass spheres are spread on to the water surface as dry powder. The particles are so long deposited on to the water surface, till the dense packing is obtained. The packing of glass beads on the water surface is checked with light microscopy. Sonication was used to aid the even distribution of the particles initially. However, it had the side effect that part of the particles sank down to the bottom of the Petri dish. Even distribution of the particles was more easy achievable, if after application of the particles some non water-miscible solvent such as chloroform was applied and slowly evaporated.

In the next step, the mixture of the 'oil' (= the organic monomer trimethylol propane trimethacrylate TMPTMA), photoinitiator and solvent is carefully applied by a syringe to the floating spheres. Then the composite layer is left undisturbed for 1 hour for solvent evaporation. After this, the oil is solidified and a composite layer is obtained.

The composite layers obtained using the same batch of glass beads as supplied by Supelco, but surface coated with the above mentioned three silanization agents are shown in Figure 3, the hydrophobicity of the coating increasing from top to bottom row. It is obvious from Figure 3 that the surface coating influences the position of the particles in the composite layer. The least
hydrophobic beads, coated with amino functionalities significantly protruded out towards the wa-
ter phase (Figure 3a, b). From the top, the particles are almost invisible. The particles of interme-
diate hydrophobicity, coated with methacrylate groups, protrude not so deep in to the water, but
still are not placed in the middle of the polymeric film (Figure 2 c, d). The most hydrophobic
spheres, coated with long alkyl chains are embedded in the middle of the polymeric matrix (Fig-
ure 2 e, f). Approximately similar segments of the glass beads protrude out from the top and the
bottom of the composite membrane.
Figure 3: Composite membrane with embedded glass beads coated with: a), b) APT; c), d) TPM; e), f) ODES.
These investigations show, that indeed the position of the particles within the layer can be tuned by choosing appropriate contact angles and that it was possible to find optimised conditions that give rise to symmetric embedding. The results show as well the influence of gravity. In the previously mentioned cases of sub-micrometric beads the optimum coating was silanization with silanes bearing methacrylate groups. As already mentioned gravity is expected to push the embedded particles further down towards the water subphase if their diameter is increased. Indeed in the case of the bigger beads used here the coating with methacrylate groups is not optimum any more, but gives rise to non symmetric embedding. Only choosing an even more hydrophobic coating finally restores the desired symmetric embedding.

The next step in membrane preparation is the removal of the glass beads. In case of silica colloids used earlier, the removal is straightforwardly done by etching with vapours of hydrofluoric acid [16, 17, 22-23]. If quartz or silica gel is etched by hydrofluoric acid, all byproducts (water, silicon tetrafluoride) are volatile. Thus, if silica colloids are exposed to the vapours of hydrofluoric acid, they seem to disappear without leaving traces. In case of glass, however the byproducts are not only non volatile (NaF, KF) but even non water soluble (CaF$_2$). Thus dry etching via gaseous hydrogen fluoride is not suitable and even was not attempted. In a first series of experiments the glass beads were etched with diluted hydrofluoric acid. The hope was that the soluble byproducts would dissolve while the non soluble ones might form small colloidal fragments that do not adhere to the remaining membrane, but are washed out nevertheless. The last part of this assumption however did not come true. The result of etching just by diluted hydrofluoric acid is shown on Figure 4. As can be seen from these images the spherical beads are destroyed. However, in a significant number of pores one can clearly see additional material, most likely precipitated byproducts from the etching process. These precipitates were analysed via electron beam micro analysis and the estimated elemental composition was in agreement with calcium fluoride.

![Figure 4: Remaining byproducts after etching with pure hydrofluoric acid.](image-url)
In a second series of experiments this calcium fluoride was washed out afterwards with diluted sulphuric acid, presumably converted into calcium sulphate, which is soluble enough to be washed out. The porous membranes are then transferred on the water surface and then are several times washed. As has been shown later in other experiments, actually one can replace this two step procedure by a one step procedure using a mixture of highly diluted hydrofluoric acid and sulphuric acid [24]. The porous membranes shown here in Figure 5 were obtained using this two step procedure.

In Figure 5a and b are shown porous membranes after removal of glass beads coated with APT. One can expect that after removal of the glass beads, different pore diameter at the top and at the bottom of the membrane will be obtained depending on the position of the beads within the layer. After removal of the less hydrophobic beads from the composite layer, only few pores are opened from the top and the big opening are visible from the bottom. The pores at the top of the membrane have sharp edges and look more like broken lids than like a thin round iris moulded form the particles that can be expected if the particles really penetrate through.

When the particles are coated with silane with methacrylate group, the pore opening at the top of the membrane increase and there are occasionally round openings visible, but still there the pore diameters at the top is much smaller than the diameter at the bottom (Figure 5 c, d). The pores at top of the membrane have approximately 30 µm in diameter. But still some of the pores are still not opened. This latter fact may be due to size dispersity of the glass beads which caused differences in the protrusion from the matrix. Inside the pores the smaller windows at the contact places between glass beads are visible. This indicates that the particles touch each other.

The pores became symmetrical when the beads are coated with the most hydrophobic silane - ODES. Their sizes are equal at the top and at the bottom of membrane and they are in range of 60-70 µm. On the walls of the pores are the small windows as in the film after removal of the TPM coated beads, but now these openings are in the middle of the height of the membrane.
Figure 5: Porous membranes after removal glass beads coated with a), b) APT; c), d) TPM; e), f) ODES
3.3. Conclusions

It has been shown, that the process of preparation of microsieves that previously was limited to pores not larger than one micrometer can be extended to the preparation of sieves having pore diameters of 70 µm. This was feasible by using commercially available glass beads instead of silica colloids and readjusting parameters like surface coating and etching procedures. It was observed that the surface coating of the glass beads influenced their position in the polymeric layer (see Figure 6). In addition the increased effect of gravity was visible: in order to position particles in the centre of the membrane and thus obtain symmetric pores, a significantly more hydrophobic coating was needed than in the case of small colloids.

These porous membranes have high porosity and good mechanical stability. They can be lifted off the water surface easily without shattering, are self supporting and can be handled by hand. They can be used as a supportive structure for another sieve like structure but with smaller pore sizes.

Figure 6: Different pores size diameters and corresponding coating of glass beads.
3.4. Experimental part

3.4.1. Preparation of glass beads coating

3 g of glass beads (Supelco) of 75 µm diameter are cleaned for 5 minutes in a mixture of 35% H₂O₂ and 96% H₂SO₄ (1 : 3 by volume) at the elevated temperature that occurred due to the heat of mixing of the two liquids. Then, they are rinsed in purified water (cleaned using a millipore water treatment system, residual organic carbon content < 5 ppb) and dried in an oven at normal pressure at 140°C for 2 hours. After this, they are immersed in 25 ml of a 10 mM solution of (3-aminopropyl)triethoxysilane (APT 0.25 mmol = 0.0448g) in toluene (technical grade) over night. Then they were washed three times with toluene and twice with acetone. The same procedure is used to prepare glass beads coated with [3-(methacryloyloxy)propyl] trimethoxysilane (TPM, 0.25 mmol = 0.0621g) and with n-Octadecyltriethoxysilane (ODES, 0.25 mmol = 0.1041 g)

Figure 4: Glass beads with 75 µm in diameter.
3.4.2. Membranes preparation.

Hydrophobized glass beads are spread as dry powder on the water surface of a partly filled plastic Petri dish of 5.4 cm diameter until a complete dense coverage was obtained. Dense packing of the beads was facilitated by applying several droplets of chloroform onto the 'dry' layer of beads and allowing it to evaporate. The complete coverage of the surface with a monolayer of beads was confirmed by light microscopy. Then a solution of trimethylolpropane trimethacrylate (TMPTMA, 15.2% by weight with respect to the whole solution) and benzoinisobutylether (3.1% by weight with respect to the whole solution) in hexane is applied to the surface with a Pasteur pipette. After evaporation of the volatile solvents (about 15 minutes) the monomer was cross-linked by irradiation with UV-light of 250 nm wavelength (low pressure mercury arc lamp, Umex Co., Germany, 250 nm wave length, intensity 0.0798 W/cm²). (Caution! Ultraviolet radiation of this wavelength and intensity is dangerous to the eyes, it may be used only in closed compartments that exclude the possibility of stray light reaching unprotected eyes). Then the solidified composite film floating on the water surface is transferred into a plastic Petri dish and dried in normal air within one hour. The film thus obtained is self supporting. To remove the glass beads, this film is transferred onto the surface of hydrofluoric acid 40% HF, afterwards the membranes were transferred to the surface of diluted H₂SO₄ (a few droplets of concentrated H₂SO₄(98%) per 100ml of purified water). After 12 hours, the film was transferred to a water surface and washed there with millipore water.

Table 1: The exact amounts of glass beads, monomer and photoinitiator solution applied to the water surface.

<table>
<thead>
<tr>
<th>Coating of particles</th>
<th>Spreading solution (TMPTMA and benzoinisobuthylethe in hexane) [g]</th>
<th>Glass beads [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>APT</td>
<td>0.3674</td>
<td>0.2826</td>
</tr>
<tr>
<td>TPM</td>
<td>0.3674</td>
<td>0.27</td>
</tr>
<tr>
<td>ODES</td>
<td>0.3674</td>
<td>0.2809</td>
</tr>
</tbody>
</table>
3.5. References

Chapter 3  Porous membranes with pores in micrometer range

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Chapter 4
Asymmetric membranes

4.1. Introduction

When a mixture of hydrophobized silica particles with an oil is applied on a water surface, a hybrid monolayer is obtained in which particles adhere to the water surface and the oil fills the free spaces between particles [1]. After solidification of the oil, a composite membrane is obtained, where particles protrude out from the top and the bottom of the polymeric matrix. By changing the surface coating of the particles, their position in the polymeric layer can be changed; a hydrophobic (hydrophilic) coating will increase the tendency of particles to adhere to the air/oil (oil/water) interface [2]. After solidification of the polymeric matrix, the composite membrane can be transferred to any desired substrate. Selective etching of the particles with hydrofluoric acid yields porous membranes with thicknesses in the range of 70 - 80% of the particle diameter. They have concave pores and within the pore walls there are small openings at the contact places where particles touch each other [3]. Porous membranes after synthesis are easy to transfer to any desired substrate. However, the most interesting membranes with pore diameter of 50-100 nm are too fragile to put them on the porous supportive structure with micrometer opening and to operate them in pressure filtration. Therefore it is necessary to give these membranes an additional support.

In cases where membranes have to be thin for performance but are too fragile, one very efficient technology is applied - so called asymmetric membranes. The asymmetric membrane is
composed of a thin selective layer (porous or dense) which is supported by porous sublayer [4]. Depending on the point of view, the structures created by Cees von Rijn via photolithography [5] might already be regarded as asymmetric membranes but their construction is comparatively elaborate. There are more simple ‘chemists approaches’ to asymmetric membranes, albeit none that yield micro sieve like structures.

The most often used method for the preparation of asymmetric membranes is immersion precipitation [6-15]. In this technique the polymer is dissolved in a good solvent or in a mixture of a good solvent and a nonsolvent. The nonsolvent for the polymer should be miscible with the solvent in which the polymer is dissolved. The polymer solution is spread by doctor blading onto a supportive structure and then immersed into a nonsolvent. The speciality of this process is that it creates a porous polymer layer. The pores sizes varying with distance from the top surface. Often the top part simply has a porosity/pore size that gradually changes towards a less or more fine morphology at the bottom. Depending on the process this can give rise to morphologies that are less coarse at the top than at the bottom and vice versa. Such membranes may be used for filtration [4, 16-17]. In extreme case the top is non porous but supported by a porous bottom part. Such membranes are suitable for chemical separation [18-25]

There are several parameters which have influence on the membrane morphology: the polymer concentration, choice of the solvent - nonsolvent system, the composition of the polymer solution and the composition of the immersion bath, the molar mass distribution and the temperature of the polymer solution. To obtain asymmetric membranes with dense top layers, the density of the polymer solution in the upper part of the deposited layer needs to be increased. This can be obtained if diffusion of the solvent out of the polymer solution is fast in comparison to the diffusion of the nonsolvent from the coagulation bath into the polymer solution. This can be done by immersion in a nonsolvent that has low affinity to the solvent, and thus only a weak gradient in chemical potential coupled to concentrations gradients. Another possibility is to cause so called delayed demixing, which appears when polymer is dissolved in a solvent as good as possible, in this case precipitation of the polymer occurs at high polymer concentration and at later time, increasing the density of the top layer. Cellulose acetate [7-8, 23] and polysulfone [9-12] are the two most often used materials for the asymmetric membrane preparation.

Another technique to obtain an asymmetric structure in the membrane is direct deposition of a thin film onto a porous supportive structure with coarse morphology. The most often used
methods for these film preparations are: dip [16, 18-20, 23], spray [17, 22], spin coating [21, 24],
grafting [26], chemical vapour deposition, plasma [27] and interfacial polymerization [25, 28].

Dip, spray and spin coating are processes where a polymer solution is applied onto a
course porous substrate and after solidification a membrane with fine structure on top of the po-
rous membrane is obtain. To prevent penetration of the polymer solution into the coarse struc-
tures the contact angles need to be controlled. There are two possibilities to obtain it, first by sur-
face treatment of the substrate and adjusting the contact angle at the liquid/air interface; second
by filling the pores with suitable liquid and adjusting the contact angle at the liquid/liquid inter-
face.

During grafting, chemical vapour deposition and interfacial polymerization, surface reac-
tions take place. A homogenous coating of the entire coarse structure is obtained when the reac-
tion is surface controlled, and a skin layer only on top of the coarse structure will be formed when
the reaction is controlled by diffusion. Interfacial polymerization has elements of both above
mentioned processes, because first two liquids are taken into contact and the reaction takes place
on the interface between them and the precipitation of the polymer is limited by diffusion of the
monomers.

As already mentioned in the previous chapters, a mixture of oil and particles applied to
water surface may form layers, which can be used to prepare porous membrane. If such an
amount of oil is used that the oil layer thickness exceeds the particles diameter, they usually ad-
sorb to one of the two interfaces of the oil.

Thus, the idea pursued here, is to spread two sorts of particles in one stroke and place
them into the desire interface by giving them appropriate surface properties (see Figure 1).
Chapter 4  Asymmetric membranes

If this idea is going to work, one needs particles of different sizes that preferentially adsorb to either the top or the bottom interface. It has been shown that the position of particles in the polymeric layer can be tuned by surface coating [2]. Thus, it can be expected that spreading of a mixture of hydrophilic and hydrophobic particles with appropriate amount of oil yields a double layers structure composed of one monolayer at the air/oil interface and second at the water oil interface. If the amount of oil will be small enough, the hydrophobic particles which adhere to the air interface will touch hydrophilic particles which are at the water/oil interface. After solidification of the oil, the removal of the particles from the polymeric layer should create pores at the top and at the bottom of the matrix. If the idea is going to work, one needs in addition that openings or 'windows' form at the contact places between the smaller and the bigger particles. The

Figure 1: Preparation of asymmetric membranes.
formation of such windows however seems to be no problem, at least in the case of densely packed monodispersed particles it has been observed almost routinely by our group and others. The structure finally obtained is expected to have higher mechanical stability due to the bigger thickness of the polymeric film.

4.2. Membranes preparation

To achieve the asymmetric structure detailed above, a mixture of two types of particles, a polymerizable non volatile oil, a photoinitiator and a volatile solvent is applied to a water surface, then the volatile solvent is evaporated and the oil is solidified via photo-polymerization. The resulting membranes are imaged before and after removal of the particles via scanning electron microscopy.

The structures obtained will depends on the contact angles and the amount of particles and oil applied (see Figure 2).
Figure 2: Variation of the contact angle of the particles at the water/oil/particles interfaces and the amount of oil.

For these experiments silica particles are chosen because they can be easily surface modified and easily removed via etching with hydrofluoric acid.

The smaller particles, Si-PFOTE, are modified with 1H,1H,2H,2H-perfluorooctyltriethoxysilane that give them a contact angle at the air/oil/particles interfaces ($\theta_{a/o/p}$) at around 56 ° and the affinity to the top surface. The larger particles shall have an affinity towards the bottom interface and in addition their contact angles at this interface shall be varied.
with this interface. Thus, two sets of large particles, varying in surface coating are used. The first set of particles, Si-TPM, has a diameter of 470 nm and second, Si-APT, a diameter of 635 nm, and their surfaces are modified with TPM - [3-(methacryloyloxy)propyl]trimethoxysilane and APT - (3-aminopropyl)triethoxysilane, giving the methacrylate and amino functionalities, respectively. The colloids modified with methacrylate groups, Si-TPM, have smaller contact angle at the water/oil/particle interface $\theta_{w/o/p}=100.78^\circ$ compared to the silica particles modified with amino groups, Si-APT, where $\theta_{w/o/p}=114.7^\circ$. The structure of the membrane, especially the possibility of contact between the large and small particles depends on the relative amount of the oil. Thus, this parameter is varied as well (see Figure 2).

Figure 2 shows the possible variations of the membrane structure. In the left column are shown scenarios for the mixture of smaller extremely hydrophobic particles and bigger colloids which surface is modified with less hydrophobic agent. The right column shows the possible scenarios for mixture of the same smaller particles at the top of the oil layer, but in this case they are mixed with larger particles that are less hydrophobic than the particles used in the left column. In scenario “a” and “b” in the Figure 2 the smaller particles adhere to the air/oil and bigger particles to the water/oil interface, but the more hydrophobic particles in the scenario “a” protrude more to the oil phase then to the water phase. When the oil amount is decreased the larger particles that are more hydrophobic (Figure 2c) start to touch the smaller particles at the top where the second sort of larger particles coated with less hydrophobic agent are still in the distance with them (Figure 2d). The larger particles with less hydrophobic coating start to touch the smaller particles at the top when the oil amount is further decreased (Figure 2e). In this stage the surface of the membrane with more hydrophobic particles at the bottom become corrugated. The membrane that consists of the larger particles with less hydrophobic groups attached to their surface will have flat surface at the bottom and at the top (Figure 2f). Their surface will become corrugated when the oil amount will be further decreased (Figure 2h). In case of the second particles the same amount of the oil will bring smaller and bigger particles so close to each other that they will create almost a mixed monolayer instead of double layers.

To obtain the desired asymmetric membrane with small thickness and possible high number of “windows” in pores; the experiments are initially conducted with mixture of small and large particles that are modified with coatings that have the biggest chemical contrast. For this reason extremely hydrophobic particles Si-PFOTE and the larger, most hydrophilic particles Si-APT are mixed with very less amount of oil and are applied to the water surface and after solvent...
evaporation the oil is solidified. This corresponds to scenario “h” in the Figure 2. The overall mass ratio oil to particles is 1:10.

The results are shown in Figure 3. On the overview pictures (Figure 3 a, b) one can recognize that the smaller 240 nm in diameter spheres are visible from the top and 635 nm in diameter particles from the bottom. In the Figure 3c, it can be seen that monolayer of the spheres with more hydrophobic groups attached to their surface is visible behind the bigger particles at the bottom side of the membrane. The top and bottom views of the composite membrane (Figure 3 c, d) indicate that hydrophilic particles adhere to the water and hydrophobic particles to the air. In the side view pictures (Figure 3 e, f, g) of the composite membrane can be seen that only smaller particles are embedded in polymeric film and the bigger particles were mostly immersed in the water. Figures 3 g shows that the top layer is corrugated and at the same time consists only of the smaller colloids.
Figure 3: SEM images of composite membrane with embedded 240 nm in diameter silica particles coated with PFOTE and 635 nm in diameter silica colloids coated with APT (monomer : particles mass ratio 1:10); a) overview picture b) overview picture with upside down orientation; c, d, e-bottom and top views; e-g) side views.

In order to create the desired porous membrane the particles are removed via etching with hydrofluoric acid, the resulting structures are shown in the Figure 4. After etching, only smaller pores are visible from the top (Figure 4 a, b). There are also bigger pores which are created due to the fact that two or three particles are connected with each other and they template irregularly shaped pores. Almost each of the smaller pores have a small window inside. These openings are very often placed on the side of the bottom part of the pores. This indicates that bigger particle at the bottom are in contact with more than one smaller particle. The membrane is approximately 150 nm thick. In Figure 4c, d can be seen that the bigger pores are rather shallow. This is the re-
result of the shallow embedding due to the high contact angle water/oil/particle (measured into the oil phase) already discussed in context of the Figure 3e.

Figure 4: SEM images of porous membrane after removal of 240 nm in diameter silica particles coated with PFOTE and 635 nm in diameter silica colloids coated with APT (monomer : particles ratio 1:10); a, b) top views; c, d) side view.

These experiments show that the mixture of two sorts of particles with opposite surface properties applied with less amount of the oil onto the water surface lead to the composite membrane where only smaller particles are embedded in the oil and hydrophilic particles at the bottom protrude to the water phase. After removal of the colloids the membrane is relatively thin (approximately 150 nm) and with less number of “windows” in pores.
To improve the membrane structure, the larger particles should be deeper immersed in the polymeric matrix and the membrane thickness should increase. For that reason in the next experiments instead of the Si-APT particles with amino groups attached to the surface, the Si-TPM particles with methacrylate groups on the surface and with smaller contact angle at the water/oil/particles interfaces ($\theta_{\text{w/o/p}} = 100.78^\circ$) are used. To obtain the thicker membrane the mass ratio oil to particles is increased to 1:8.7. That means that we moved from the scenario “h” to “e” in Figure 2.

The composite membranes are shown in Figure 5. Bottom view shows that also smaller particles are in between the larger colloids (Figure 5a, b). In the top view of the membrane one can recognize that not only smaller particles but also bigger particles are protruding out from the polymeric film (Figure 5c, d). Less hydrophobic spheres are bit lower placed in the matrix than the smaller ones. The same phenomena is easily to recognize in the side view picture that smaller as well bigger colloids create two layers, but the membrane surface is even more corrugated than the membrane with embedded Si-APT particles.
Figure 5: SEM images of composite membrane with embedded 240 nm in diameter SI-PFOTE silica particles and 470 nm in diameter Si-TPM silica colloids (monomer : particles mass ratio 1:8.7); a, b) bottom views; c, d) top views; e, f) side views.
In Figure 6 are shown the porous membranes after etching with hydrofluoric acid. After the removal of the particles one can see predominately smaller pores at top the bigger pores at the bottom, respectively, however, there are as well smaller ones at the bottom and bigger ones at the top. The shape and size of the pores indicate that particles do not create two pure separated layers of particles but that these layers are to some extend mixed. Most of pores at bottom of the membrane have four windows (Figure 6a, b). This indicates an intense contact between the two layers and to some extend reflects the corrugation observed in the composite layers before etching.
To reduce the tendency of the particles to form mixed layers the amount of oil is increased to such extend that the top surface of the membrane won’t be corrugated. That means that the scenario “c” in Figure 2 has to be reached. The theoretical mass ratio oil to particles in the scenario in Figure 2c, where particles from the top layer start to touch particles at bottom is 1:5.8 (see appendix). This value was used in the next experiments. The results are shown in Figure 7.

The experiments show that with this ratio the smaller particles protrude out to the air and the bigger particles to the water phase. The top and the bottom view indicate that spheres with smaller as well as with bigger diameter create hexagonally packed monolayers (Figure 7 a, b). The membrane surface on the both interfaces is not corrugated. On the side view image it can be recognized that almost all the particles are embedded in the polymeric matrix and only small segments of spheres protruded out from the top and the bottom (Figure 7 c, d). The membrane thickness is around 600 nm.
Figure 7: SEM image of Composite membrane with embedded 240 nm in diameter Si-PFOTE silica particles and 470 nm in diameter Si-TPM silica colloids (monomer : particles mass ratio 1:6); a) bottom view; b) top view; c, d) side views.
In Figure 8 are shown porous membranes after etching of silica particles with hydrofluoric acid. After removal of the particles only small pores are visible from the top (Figure 8c, d) and bigger pores form the bottom (Figure 8a, b). The pores are concave and inside the porous small “windows” are visible. The windows diameters are in the desired range from 30 nm to 50 nm. The number of windows inside the pore indicates the number of particles which were in the contact with sphere. In some of the small pores, there are clearly windows visible, but not in all of them. Correspondingly the number of windows in the large pores (approximately 1.5 windows per pore) is significantly reduced compared to the average of four windows visible in Figure 6. Thus, there are two trends that need to be balanced: a lower amount of the oil and more hydrophobic coating of particles at the bottom increase the contact between the particles of the two layers and increase the Laplace pressure inside layer thus giving rise to a more close packing. At the same time however, it counteracts the separation of the two types of particles into two separate layers, at the extreme giving rise to a mixed monolayer instead of the desired hierarchical structure.
Figure 8: SEM images of porous membrane after removal of 240 nm in diameter silica particles coated with PFOTE and 470 nm in diameter silica colloids coated with TPM (monomer : particles mass ratio 1:6) ; a, b) bottom views; c, d) top view.

As already mentioned before; all membranes were prepared on the surface of the water filled Petri dish. The solution of particles and monomer in solvents were spread with a syringe in the form of droplets. When the first droplets touched the water surface then both sorts of particles created mixed monolayer. This monolayer was obtained mostly at the rim of the Petri, and when the solution was added further on, the double layer was obtain. Images of the monolayer are shown in Figure 9. The double layer and monolayer of particles could be recognized even with unaided eye. The areas of the water that were covered with double layer appeared white, and the places where only monolayer existed reflected the light only from the certain angle. Usually the
60-80% of the whole area of the Petri dish was covered by double layer and on the rest monolayer was floated.

Figure 9: SEM images of composite membranes with embedded Si-APT and Si-PFOTE (mass ratio monomer : particles 1:10). Shown is the 'water-side' of the membrane. The large less hydrophobic particles (yellow circle) protrude significantly into the water phase, while the smaller strongly hydrophobic particles (red circle) are barely visible. The large particles in this image acquired in addition some nanoscopic protrusion (violet circle), which are not to be confused with the hydrophobic particles.
4.3. Conclusions

Particle assisted wetting is a new method of asymmetric membranes preparation. Spreading mixtures of two kinds of particles with suitable surface properties with the right amount of oil onto a water surface yields composite layers in which the more hydrophobic particles protrude from the top and less hydrophobic spheres from the bottom. Solidification of the oil and removal of the colloids with hydrofluoric acid yields asymmetric membranes with pores in the range of 30-50nm. There is a correlation between the membrane structure and the contact angles respectively volume ratios oil/particles. In general, low contact angles (measured into the oil phase) give rise to thicker membranes. Concerning the amount of oil there are two effects that need to be balanced: too low a volume of oil generates a too large Laplace pressure on the particles and this gives rise to defects in the order of particles and in the final membrane. If too much oil is chosen there is not enough force to press the particles together and the number of windows between pores is reduced.
4.4. Experimental part

4.4.1. Particles synthesis and coating

Particles are synthesized in a Stöber type synthesis and subsequently coated in a one pot procedure.

Three sorts of particles are prepared. The particles are coated by treatment with (3-aminopropyl)triethoxysilane (Sigma Aldrich, 99%), [3-(methacryloyloxy)propyl] trimethoxysilane (Sigma Aldrich, 98 %), and 1H,1H,2H,2H-perfluorooctyltrietoxysilane (Sigma Aldrich, 98 %) respectively.

At the beginning of the synthesis, tetraethyl orthosilicate (Sigma Aldrich 98%), ammonia (25%) (technical grade) and water are added to 200 ml of ethanol (98 %, technical grade) in a 500 ml round bottom flask at constant stirring and at room temperature (step I). After four hours again TEOS, ammonia, water are poured to the reaction medium (step II). Finally after another hour the suitable silane coupling agent is added (step III). After 5.5 hours ammonia is evaporated at reduced pressure with a water jet aspirator pump, then water and ethanol are removed with a rotary evaporator at reduced pressure generated by a rotary pump. Then crude white powder is subsequently washed with ethanol with five cycles of centrifugation with speed of 6000 rpm. After washing process, dispersion of a mass fraction of 20 % of particles in ethanol is prepared.

To obtain different sizes of particles; various amount of TEOS, water, ammonia are added during each step of synthesis as given in table 1.
Table 1: The amounts of TEOS, water, ammonia and silane coupling agents added during synthesis of particles.

<table>
<thead>
<tr>
<th>Product name</th>
<th>Step I</th>
<th></th>
<th></th>
<th>Step II</th>
<th></th>
<th></th>
<th>Step III</th>
<th>Silane coupling agent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water</td>
<td>ammonia</td>
<td>TEOS</td>
<td>water</td>
<td>ammonia</td>
<td>TEOS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-PFOTE</td>
<td>1 ml</td>
<td>16 ml</td>
<td>9 ml</td>
<td>0.5 ml</td>
<td>2 ml</td>
<td>1 ml</td>
<td>0.5 ml</td>
<td>1H,1H,2H,2H-perfluoroctyltriethoxysilane</td>
</tr>
<tr>
<td>Si-TPM</td>
<td>1 ml</td>
<td>25 ml</td>
<td>8 ml</td>
<td>1 ml</td>
<td>2 ml</td>
<td>1 ml</td>
<td>0.5 ml</td>
<td>[3-(methacryloyloxy)propyl] trimethoxysilane</td>
</tr>
<tr>
<td>Si-ATP</td>
<td>1 ml</td>
<td>28 ml</td>
<td>8 ml</td>
<td>1 ml</td>
<td>4 ml</td>
<td>1 ml</td>
<td>0.5 ml</td>
<td>(3-aminopropyl) triethoxysilane</td>
</tr>
</tbody>
</table>

Particles sizes and shapes are characterized with scanning electron microscopy (NanoNovaSEM, Company FEI). A droplet of the dispersion of particles in ethanol 0.05 % (weight fraction) is deposited onto a silicon wafer and imaged with SEM. The mean diameter of particles modified with PFOTE is 238 nm and the standard deviation is 12 nm. Particles coated with APT are 634 nm in diameter and the standard deviation is 25 nm. Colloids that are modified with TPM are 474 nm in diameter and the standard deviation is 16 nm. The analysis based on the 80 particles of each sorts. Given the obtained standard deviations, rounded values (240 nm, 635 nm, 470 nm) are used throughout the descriptive parts of this chapter.
Chapter 4  Asymmetric membranes

Figure 10: Silica particles; a) 240 nm in diameter; b) 470 nm in diameter, c) 635 nm in diameter.
4.4.2. Synthesis of asymmetric membranes.

The asymmetric membranes are synthesized with two combinations of particles. First membranes are prepared from mixture of silica particles with 635 nm in diameter coated with APT and particles with 240 nm in diameter coated with PFOTE. For the synthesis of the second series of membranes, the particles coated with TPM with 470 nm in diameter are mixed also with the most hydrophobic particles with 240 nm in diameter.

The membranes are prepared always with the same procedure with variations detailed in tables 2-4. First, appropriate amounts of small and large particles needed to obtain a closed packed monolayer of these particles are calculated. The corresponding amounts of the dispersions of known mass fractions of each of the particles are mixed. The ethanol dispersion of smaller particles (20% by weight) is mixed with ethanol dispersion of bigger particles (20% by weight). Then this mixture of two dispersions of particles is redispersed in a mixture of ethanol/chloroform (both are technical grade) (1:4, per volume), ethyl butyrylacetate (98% Sigma Aldrich). In the next step the solution of trimethylolpropane trimethacrylate (technical grade, Sigma Aldrich) in ethanol and chloroform (both are technical grade) (1:4 by weight) and benzoinisobuthyl ether (Sigma Aldrich) are added to dispersion of particles. The exact compositions of the spreading solutions are given in tables 2 – 4. Then all the components are spread with a syringe and needle onto the surface of purified water that was filled into a glass Petri dish of 5.4 cm diameter. After spreading, the Petri dish is covered with a polystyrene lid and left for 12 hours. Then the Petri dish is opened for 30 minutes to evaporate the solvents and finally monomer is cross-linked with UV-light (low pressure mercury lamp UMEX Dresden with emission predominantly of 250 nm wave length, intensity 0.0798 W/cm\(^2\)). (**Caution!** Ultraviolet radiation of this wavelength and intensity is dangerous to the eyes, it may be used only in closed compartments that exclude the possibility of stray light reaching unprotected eyes). The solidified composite membranes are transferred to silicon wafer. Etching of the particles is done in such a way that the membranes on the silicon wafers are placed in a plastic Petri dish and then 1 droplet of hydrofluoric acid (40%) (Fluka) (**Caution!** Hydrofluoric acid is toxic and corrosive and should be handled only by trained personnel aware of the dangers associated with the use of this chemical!) is applied near the membrane. Then the Petri dish is covered with a polystyrene lid and kept for 15 minutes. After this time the hydrofluoric acid is neutralized with saturated calcium acetate solution and the etched membrane taken out of the dish.
### Table 2: Composition of membrane with monomer : particles ration 1 : 10 (by weight)

<table>
<thead>
<tr>
<th>Components</th>
<th>Mass [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica particles Si-PFOTE, 240 nm in diameter, coated with PFOTE in ethanol 20% (weight)</td>
<td>0.0055</td>
</tr>
<tr>
<td>Silica particles Si-APT, 635 nm in diameter, coated with APT in ethanol 20% (weight)</td>
<td>0.0145</td>
</tr>
<tr>
<td>3 % (by weight) TMPTMA in ethanol : chloroform (1:4 by weight)</td>
<td>0.0154</td>
</tr>
<tr>
<td>Benzoinisobuthylether</td>
<td>0.0002</td>
</tr>
<tr>
<td>Ethyl butyrylacetate</td>
<td>0.0042</td>
</tr>
<tr>
<td>Ethanol/chloroform mixture (1:4 by weight)</td>
<td>0.3878</td>
</tr>
</tbody>
</table>

### Table 3: Composition of membrane with monomer : particles ration 1 : 8.7 (by weight)

<table>
<thead>
<tr>
<th>Components</th>
<th>Mass [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica particles Si-PFOTE, 240 nm in diameter, coated with PFOTE in ethanol 20% (weight)</td>
<td>0.006</td>
</tr>
<tr>
<td>Silica particles Si-TPM, 470 nm in diameter, coated with TPM in ethanol 20% (weight)</td>
<td>0.017</td>
</tr>
<tr>
<td>3 % (by weight) TMPTMA in ethanol : chloroform (1:4 by weight)</td>
<td>0.01459</td>
</tr>
<tr>
<td>Benzoinisobuthylether</td>
<td>0.00018</td>
</tr>
<tr>
<td>Ethyl butyrylacetate</td>
<td>0.0038</td>
</tr>
<tr>
<td>Ethanol/chloroform mixture (1:4 by weight)</td>
<td>0.3633</td>
</tr>
</tbody>
</table>

### Table 4: Composition of membrane with monomer : particles ration 1 : 6 (by weight)

<table>
<thead>
<tr>
<th>Components</th>
<th>Mass [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica particles Si-PFOTE, 240 nm in diameter, coated with PFOTE in ethanol 20% (weight)</td>
<td>0.0045</td>
</tr>
<tr>
<td>Silica particles Si-TPM, 470 nm in diameter, coated with TPM in ethanol 20% (weight)</td>
<td>0.0081</td>
</tr>
<tr>
<td>3 % (by weight) TMPTMA in ethanol : chloroform (1:4 by weight)</td>
<td>0.014</td>
</tr>
<tr>
<td>Benzoinisobuthylether</td>
<td>0.0002</td>
</tr>
<tr>
<td>Ethyl butyrylacetate</td>
<td>0.0116</td>
</tr>
<tr>
<td>Ethanol/chloroform mixture (1:4 by weight)</td>
<td>0.4059</td>
</tr>
</tbody>
</table>
Appendix

As shown in Figure 2 the volume ratio of oil to particles influences the structure. One especially important structure is double layer in which the two interfaces are flat and the two layers of spheres touch each other. For this structure calculation of the volume ratio particles/oil is straightforward.

Figure 11: Mixed layer of hydrophilic (red) and hydrophobic (yellow) particles embedded in the oil (green) floating on the water surface.

The thickness of the polymeric layer is defined by the particles immersion in the polymeric layer. The immersion of the smaller particles is defined by the contact angle ($\theta_{a/o/p}$) at the air/oil/particle and the bigger particles by the contact angle ($\theta_{w/o/p}$) at the water/oil/particle interfaces.

Figure 12: Contact angles at the air/oil/particle interface and at the water/oil/particle interface.
Table 5: Contact angles of spherical particles at the air/TMPTMA and at the water/TMPTMA interfaces [29].

<table>
<thead>
<tr>
<th>Particles</th>
<th>(\theta_{a/o/p})</th>
<th>(\theta_{w/o/p})</th>
</tr>
</thead>
<tbody>
<tr>
<td>240 nm, coated with PFOTE</td>
<td>56.43°</td>
<td>42.35°</td>
</tr>
<tr>
<td>470 nm, coated with TPM</td>
<td>9.5°</td>
<td>100.78°</td>
</tr>
<tr>
<td>635 nm, coated with APT</td>
<td>6.65°</td>
<td>114.7°</td>
</tr>
</tbody>
</table>

A volume of immersed part of particles in the oil and a volume of the oil between them for the top and the bottom layers respectively is calculated. Particle diameters at the top and at the bottom differ from each other, so the volume of particles per area, that is covered by them and also the volume of the oil that remains between particles divided per area are calculated. Afterwards the calculated values for the top and the bottom layers will be added and finally the volume ratio of all particles to the oil will be obtained.

It is assumed that all particles are spherical, so their volume is given as

\[
V_i = \frac{4}{3} \pi R^3
\]  

It is also assumed that particles at each interface are hexagonally packed.

![Hexagonal packing of spheres with the same diameter.](image)

Then the area per particle is:

\[
\frac{A}{n} = D \cdot x = D^2 \cdot \sin 60^\circ = \frac{\sqrt{3}}{2} \cdot D^2 = A(R) = 2 \cdot \sqrt{3} \cdot R^2
\]  

Then the ratio of particle volume to the area occupied by this particle is expressed as:

\[
K_i(R, \theta) = \frac{V_i}{A(R)} = \frac{2 \cdot \pi \cdot R}{3\sqrt{3}}
\]
At each of the interfaces, the immersion of particles is defined via contact angle. Then the part of particle that is immersed in the oil is:

\[
V_p(R, \theta) = \frac{4 \cdot \pi}{3} \cdot R^3 \cdot \left[1 - \frac{(1 - \cos \theta)^2 \cdot (2 + \cos \theta)}{4}\right]
\]  

(4)

The ratio of the volume to the area is given by:

\[
K_2(R, \theta) = \frac{V_p(R, \theta)}{A(R)} = \frac{2 \cdot \pi \cdot R}{3 \cdot \sqrt{3}} \cdot \left[1 - \frac{(1 - \cos \theta)^2 \cdot (2 + \cos \theta)}{4}\right]
\]  

(5)

The thickness of the oil layer in which the particle is immersed is given as:

\[
H = K_3(R, \theta) = \frac{V_p(R, \theta)}{A(R)} = R \cdot (1 + \cos \theta)
\]  

(6)

The oil amount in composite monolayer is given as the volume of the oil without particles (the thickness of this layer is \(H\)) minus the volume of the immersed part of the particle in the oil and this can be expressed as

\[
K_4(R, \theta) = K_3(R, \theta) - K_2(R, \theta) = R \cdot \left[1 + \cos \theta - \frac{2 \cdot \pi}{3 \cdot \sqrt{3}} \cdot \left[1 - \frac{(1 - \cos \theta)^2 \cdot (2 + \cos \theta)}{4}\right]\right]
\]  

(7)

When we apply equation number 7 and 3 for each sort of particles then the volume ratio of the oil to the particles is given as:

\[
\left(\frac{V_p}{V_o}\right)_{\text{theoretical}} = \frac{K_1(R_{\text{big particles}}, \theta_{\text{wop}}) + K_1(R_{\text{small particles}})}{K_4(R_{\text{big particles}}, \theta_{\text{wop}}) + K_4(R_{\text{small particles}}, \theta_{\text{wop}})}
\]  

(8)

To get the mass ratio of the oil to the particles the volumes ratio need to be multiplied via density ratios of the oil and the particle

\[
\frac{M_p}{M_o} = \frac{V_p}{V_o} \cdot \frac{\rho_p}{\rho_o}
\]  

(9)

\[
\left(\frac{M_p}{M_o}\right)_{\text{theoretical}} = \frac{K_1(R_{\text{big particles}}, \theta_{\text{wop}}) + K_1(R_{\text{small particles}})}{K_4(R_{\text{big particles}}, \theta_{\text{wop}}) + K_4(R_{\text{small particles}}, \theta_{\text{wop}})} \cdot \frac{\rho_p}{\rho_o}
\]  

(10)

\(R_{\text{big particles}}, \theta_{\text{wop}}\) - radius and contact angle of the bigger particles

\(R_{\text{small particles}}, \theta_{\text{wop}}\) - radius and contact angle of the smaller particles

For the mixture of particles coated with PFOTE and TPM the volume and mass ratios of particles to the oil are:
\[
\left( \frac{V_p}{V_o} \right)_\text{theoretical} = \frac{K_1(470\text{nm}) + K_1(238\text{nm})}{K_4(470\text{nm, 100.78°}) + K_4(238\text{nm, 56.43°})} = 2.9
\]

(11)

\[
\left( \frac{M_p}{M_o} \right)_\text{theoretical} = \frac{K_1(470\text{nm}) + K_1(240\text{nm})}{K_4(470\text{nm, 100.78°}) + K_4(240\text{nm, 56.43°})} \cdot \frac{1.9 \frac{g}{cm^3}}{1 \frac{g}{cm^3}} = 5.8
\]

(12)
4.5. References

Chapter 5

Porous membranes with functionalized pores – silica rings.

5.1. Introduction

Surface properties of membranes play very important roles in separation processes. The hydrophobicity and hydrophilicity of the membrane have tremendous influence on the transport thorough the membrane. These effects are especially significant in adsorptive membrane (ion exchange, affinity, reverse-phase and hydrophobic interaction membranes) [1] with application in the membrane chromatography.

There are several methods to change the chemical character of the membrane surface. The most used strategy is activation of the membrane, usually done by grafting polymerization or coating.

For example microporous membranes made from polypropylene or polyethylene were modified by radiation induced grafting polymerization. This introduced ion exchange groups like: amine, methoxy or carboxyl group which contain monomers (vinyl acetate or 2-hydroxyethyl methacrylate). Those membranes were then used as ion exchange membranes or further modified with other functional groups (glycidyl methacrylate, diethylamino, sulfonic acid group). [2-14] To make PVDF membranes less hydrophobic, the treatment with strong basic solution was needed. After this procedure fluorine and hydrogen were eliminated from the polymeric chain and active sites were generated on the surface. Then these active sites were grafted with glycine and this also allows the further synthesis with amino acids [15].
Chapter 5  Porous membranes with functionalized pores – silica rings

Another approach to change the surface properties of the membrane is coating. With this technique polypropylene hollow fibres were coated with polyvinyl alcohol [16], microporous structure of poly(ethylene oxide) blend was decorated with poly(ether sulfone) [17] and nylon with ethylene glycol diglycidyl ether [18].

There are also methods which can change only the inner pores of the membrane. One of such method is preparation of the silica nanotubes membranes [19]. In this method porous alumina is coated by silica in an acidic sol gel process (immersing into a mixture of ethanol, tetraethyl orthosilicate and HCl followed by ageing and drying). This procedure yields silica nanotubes with a wall thickness of 3 nm. The inner surface of the tubes was further “biofunctionalized” with rhodamine B isothiocyanate. The fluorescence signal of rhodamine B from the silica nanotubes was 7 times bigger than from the pure alumina membrane. This is due to the fact that the density of the hydroxyl group on sol-gel silica is higher than of the alumina surfaces.

In case of microsieve-like membranes such as those prepared in our experiments the pore functionalization via coating can lead to the synthesis of submicrometer sized rings [20].

The synthesis of submicrometer sized rings has recently attracted the attention of the scientific community due to a general interest in shaping material into various geometries [21-23] and due to several more subtle physical properties of rings of that size. Rings made from metallic or superconducting materials can give rise to persistent currents if exposed to a magnetic field [24-27]. Rings exhibit tunable plasmon resonance in the near infrared, and therefore might be used as elements in nonlinear optical devices and improved probes for surface enhanced Raman scattering [28]. Arrays of macroscopic metal rods and split rings can give rise to materials with a negative refractive index for radiation of appropriate wavelength [27]. This phenomenon - originally proven with millimeters sized structures and microwaves - might be extended to visible light, if the structure size is scaled down correspondingly.

In principle, the ring like structure can be generated using conventional photolithographic processes. However, these methods become the more complicated the smaller the diameter of the rings. For nanoscopic rings advanced methods like electron beam lithography, deep UV or X-ray lithography are necessary. The limitations of conventional photolithography can be overcome via non conventional methods. To our knowledge there are a few reports in the literature that describe different principles for the generation of rings.
The impact of a focused high energy electron beam can create craters that are surrounded by ring shaped elevation [29, 30]. Wetting phenomena can cause nanosized droplets that are surrounded by a well, to redistribute into ring shaped geometry [31, 32].

Several authors deposit metals or inorganic compounds onto nanostructured regular templates like nanoporous alumina or arrays of colloids, followed by removal of the template, sometimes occurring simultaneously with a redistribution of the material [28, 33-36]. Another elegant technique based on the redistribution of material is displacement of polymers by droplets of solvents [37].

In previous papers [20, 38] we reported that one can embed a monolayer of silica particles on a water surface within a thin layer of polymer in such way that the particles penetrate through both interfaces of this layer. Removal of the particles gives rise to a membrane with uniform pores. Wetting the inner walls of the pores with a liquid, followed by solidification of the liquid and selective removal of the polymer, gave rise to submicroscopic rings. In these investigations, the embedded monolayers of the particles first were transferred to a solid substrate and then the particles were completely removed within minutes via etching with hydrofluoric acid. As an alternative approach, we investigated the possibility to remove the particles already while the membrane was still floating on the water surface. We observed that the etching this time was significantly slowed, and interestingly found ring-like structures at intermediate stages of particle removal.

5.2. Pores functionalization and silica ring preparation.

Silica colloids (500 nm) were suspended in a mixture of ethanol/chloroform (1:1 by volume) photoinitiator benzinisobuthylether and the organic monomer trimethylolpropane trimethacrylate (TMPTMA). These suspensions were spread onto the surface of a water-filled plastic Petri dish, in such an amount as to yield complete coverage of the surface by the colloids, for details see [38]. After evaporation of the solvent, the organic monomer in the mixed monolayers was cross-linked with UV- light of 250 nm wavelength. This Petri dish with the solidified monolayer was placed inside a second larger Petri dish which then was covered by its lid. The solidified monolayer was exposed to the vapour of hydrofluoric acid (48%) for various time up to 5 hours and afterwards transferred to glass plates. Depending on the exposure time etching completely or partially removed the silica particles. To image the remaining silica within the
membrane, part of the sample was placed in an oven and the polymer removed by pyrolysis in air at 250°C and 500°C (30 minutes of each temperature).

Figure 1: Scheme of the preparation of porous membranes and ring shaped particles:
a) original layer of silica particles embedded in a polymeric matrix on a water surface; c, e, g) progressively advancing stages of removal of the particles via etching with hydrofluoric acid; b, d, f, h) original particles, rings, sickles, and no particles recovered after pyrolysis of the polymer.

Electron microscopy images of the structures thus obtained before and after removal of the polymer are shown in Figure 2, and a schematic interpretation of the images is shown in Figure 1.
Figure 2: Monolayer with embedded silica particles before etching and after 1.5; 3; 5 hours of etching (a, c, e, g); the same layer after removal of the polymer via pyrolysis (b, d, f, h).
Figure 2a shows the layer of silica particles embedded in the polymer after transfer to a solid substrate without any etching involved. The particles partially protrude at the top of the surface and the polymer is visible as grey regions between the individual particles. If the polymer is removed (Figure 2b), one obtains a monolayer of particles only.

After 5 hours of exposure to hydrofluoric acid, the particles are completely removed and one obtains a porous polymeric membrane, very similar to the one reported earlier (Figure 2g). After pyrolysis of the polymer, only few insignificant residues can be observed (Figure 2h).

The two most characteristic intermediate stages are shown in Fig. 2 c-b) and 2 d-e).

After 1.5 hours of etching (Figure 2 c) one observes already holes in the composite membrane, but considerably smaller than in the completely etched case of Figure 2g. After removal of the polymeric matrix, the substrate is covered with a dense array of rings. Obviously the etching selectively removed only the center of the silica particles. A close up picture of these rings is shown in Figure 3a. The overview picture in Figure 2d reveals that the wall thickness varies from ring to ring, furthermore at some places an individual ring seems to be completely removed and at a few places non centrosymmetric and even sickle shaped particles can be observed.

After 3 hours of etching (Figure 2e) the pores in the composite membrane are wider then in Figure 2c, but still not as wide as in the final stage. After removal of the polymer (Figure 2f) the predominant features on the substrate are sickle shaped particles, a significant number of particles are completely removed and there are a few rings visible.

My understanding of the creation of silica rings and sickles is as follows: during etching on the water surface, only the small part of the particles that protruded out of the polymeric layer is exposed to vapours of HF. The rest of the particles is embedded in the solidified matrix and thus shielded from the etching. Initially, the hydrofluoric acid reacts with silica on top of the monolayer and after some time as well on the bottom part through the aqueous phase. With progressing time, the etching is proceeding deeper into the silica particle and finally after 1.5 hours of exposure, the cavity etched into the top part reaches the bottom. This assumption of partial shielding of the particles from etching is further supported by high resolution SEM images of the membrane after etching, but before removal of the polymer (Figure 3b). In this image, one sees the hole etched into an individual particle, which is still surrounded by a thin “iris” of the polymer.

This mechanism alone does not explain the break of centrosymmetry and the formation of the sickles. It might be possible that the symmetry is broken by purely convective processes; on the
other hand, the gaseous silica tetrafluoride generated as a byproduct in the etching might form bubbles that cling to one side of the silica rings and thus break the symmetry. Based on the current observations it is not straightforward to draw a final conclusion.

Another unexpected feature of the process is the fact that individual particles seem to be etched at a faster rate than others. For example the wall thickness of the rings in Figure 2d varies from ring to ring and a few particles seem to be barely etched while occasional empty sites indicate the complete removal of others.

In principle, this might indicate an inhomogeneity in the composition of the particles; however it is more likely that the effect is due to a variation in the embedding. It appears that there is a considerable size variation of the polymeric “iris” attached to the rim of each of the pores.

For example in Figure 3b an almost completely etched particle is exposed to the gas phase through a rather wide opening in the matrix, while its right neighbor is exposed to the gas phase through only a comparatively small opening and is barely etched. The size variations of “iris–diameter” can as well be seen on the overview picture of a completely etched membrane shown in Figure 3c.

Most probably, this variation in “iris–diameter” is due to the fact that the predominant part of a particle is embedded in the polymeric matrix and only the very top protrudes out of the polymer as a rather shallow spherical cap. Due to the shallowness of the protrusions, small variation in particle size give comparatively large variations in the diameter of the spherical caps and as consequence result in significant variations in the “iris–diameter” see (Figure 3d). This variation in the “iris–diameter” in turn influences the etching rate of individual particles. Thus, for the preparation of uniform rings, a size distribution of the particles as narrow as possible might be necessary.
Figure 3: High resolution scanning electron microscopy picture of: a) individual silica rings b) of the membrane after 1.5 hours of etching with hydrofluoric acid, but before removal of the polymer, c) overview of a completely etched monolayer after 5 hours of etching with HF, d) schematic drawing illustrating the influence of particle size variations on the variations in “iris-diameter”
5.3. Conclusions

By partial etching of silica particles from composite membrane give rise to pore functionalization.

In conclusion, a simple method of preparation of silica rings by using a solidified organic wetting layer as a protecting material has been developed. To my knowledge, this method has not been reported before and in principle might be extended to any other material that can be etched from the gas phase.
5.4. Experimental part

Silica particles of 500 nm diameter were synthesized following Stöber’s method [39], hydrophobized by coating them with [3-(methacryloyloxy)propyl] trimethoxysilane (TPM) [40], and subsequently washed with ethanol by four cycles of centrifugation and ultrasonic dispersion.

At the beginning of the synthesis, 8 ml of tetraethyl orthosilicate (Sigma Aldrich 98%), 25 ml of ammonia (25%) (technical grade) and 1 ml of water are added to 200 ml of ethanol (98 %, technical grade) in a 500 ml round bottom flask at constant stirring and at room temperature. After four hours again 1 ml of TEOS, 2 ml of ammonia, 1 ml of water are poured into the reaction medium. Finally after another hour [3-(methacryloyloxy)propyl] trimethoxysilane (Sigma Aldrich, 98 %) is added. After 5.5 hours ammonia is evaporated at reduced pressure with a water jet aspirator pump, then water and ethanol are removed with a rotary evaporator at reduced pressure generated by a rotary pump. Then crude white powder is subsequently washed with ethanol with five cycles of centrifugation with speed of 10000 rpm. After washing process, dispersion of a mass fraction of 20 % of particles in ethanol is prepared.

Particles sizes and shapes are characterized with transmission electron microscopy (EM 400T microscope Philips, The Netherlands). A droplet of the dispersion of particles in ethanol 0.05 % (weight fraction) is deposited onto a copper TEM grid and imaged with transmission electron microscopy.

![Figure 4: Transmission Electron Microscopy image of 500 nm in diameter silica particles.](image-url)
These silica colloids (500 nm) were suspended in a mixture of ethanol/chloroform (1:1 by volume) and the organic monomer trimethylolpropane trimethacrylate (TMPTMA) (mass ratio of particles to TMPTMA = 5:1; mass ratio of particle to solvent = 1:100). These suspensions were spread onto the surface of a water-filled plastic Petri dish, in such an amount as to yield complete coverage of the surface by the colloids, for details concerning the calculation of the amount to be applied [appendix, Chapter 4]. After evaporation of the solvent, the organic monomer in the mixed monolayers was cross-linked with UV-light of 250 nm wavelength (low pressure mercury arc lamp, Umex Co., Germany). (Caution! Ultraviolet radiation of this wavelength and intensity is dangerous to the eyes, it may be used only in closed compartments that exclude the possibility of stray light reaching unprotected eyes) This Petri dish with the solidified monolayer was placed inside a second larger Petri dish which then was covered by its lid. The solidified monolayer was exposed to the vapour of hydrofluoric acid (48%) (Caution! Hydrofluoric acid is toxic and corrosive and should be handled only by trained personnel aware of the dangers associated with the use of this chemical!) for various time up to 5 hours and afterwards transferred to glass plates. Depending on the exposure time etching completely or partially removed the silica particles. To image the remaining silica within the membrane, part of the sample was placed in an oven and the polymer removed by pyrolysis in air at 250°C and 500°C (30 minutes of each temperature).
5.5. References


Chapter 5  Porous membranes with functionalized pores – silica rings


Chapter 6

Mixed matrix membranes for gas separation

6.1. Introduction

The separation of compounds out of gaseous or liquid mixtures (e.g. enrichment/depletion of oxygen out of air; depletion of condensable C4-compounds out of natural gas, separation of aliphatic and aromatic hydrocarbons out of mineral oil) has been a big challenge over the last decades. It has been shown that membrane processes can pose significant advantages compared to other separation processes, especially they might separate compounds out of azeotropic mixtures, that can not be separated by distillation and they can save a considerable amount of energy [1].

A membrane is characterised by its permeability for any specific compound considered. If the permeability is a function of the compound applied, the membrane is considered 'selective' for the compound that shows a higher permeability. The ratio between the permeabilities of two compounds is called the selectivity (or permselectivity) of the membrane. Often a satisfying selectivity is accompanied with a low general permeability and vice versa. Based on this observation Roberson plotted in 1991 the curve for oxygen/nitrogen selectivity vs. the permeability of various membranes and discovered the so called 'upper bond', a line within this diagram above which no data points were found, which signified the trade off between selectivity and permeability [2]. In the last decades there have been intense and successful research activities to "push the upper bond upward", i.e. to establish materials with improved selectivity and permeability [3-11].
Successful materials often show the common structure of having a rigid structure with comparatively large and non deformable internal voids [3-4]. The most used materials for that process are organic polymers and so called molecular sieving materials. These two kinds of materials have their merits and limitations: The organic polymers can be processed as solution or melt and show at least some degree of ductility. Therefore, they can be converted quite easily into the required form of a mechanically sturdy thin sheet. However, their rigidity and their internal free volume are limited [13-15]. Molecular sieving materials (e.g. silicalite [16], zeolite [6, 17-18], carbon molecular sieves [3-4, 19], metal organic frameworks) are highly cross-linked often regular matrices with large internal voids that are stabilized by a high density of covalent or ionic bonds [20-21]. This rigidity is of advantage for the separation process; however it inherently renders these materials brittle. This brittleness is a significant obstacle in the preparation of thin freestanding sheets of these materials and in the operation of modules comprising such thin membranes [10]. Thus, there have been attempts to combine the properties of polymers and molecular sieves by embedding molecular sieving materials in a polymeric matrix. Membranes made from such mixtures are called "mixed matrix membranes" and indeed have high selectivity and good mechanical stability [3-12].

6.2. Theoretical description of gas transport in mixed matrix membranes

Permeabilities of mixed matrix membranes composed of two distinct phases in principle may be described by three models: (i) the Maxwell model (Figure 1) for transport in a system composed of particles dispersed in a continuous 3 dimensional matrix [7, 8], (ii) serial model (Figure 2) [5, 7-8], where two phases are placed horizontal to the gas flow and (iii) parallel model (Figure 3) [5, 7-8], where two phases are placed parallel to each other and to the flux of the permeating medium. For each substance the permeability of the membrane can be calculated from the permeabilities of each of the pure phases [5, 7-8]. The detailed descriptions of Maxwell, serial and parallel models are given below.
a) Maxwell model

Figure 1: Schematic drawing of mixed matrix membrane described by Maxwell model.

In conventional mixed matrix membranes one of the two phases is confined to size limited domains that are separated from each other and are embedded within a continuous 3 dimensional matrix. The permeability of such a membrane for each compound may be predicted based on work of Maxwell who described the dielectric problem of embedded spheres and systems composed of concentric shells. It can be shown, that the problem of a substance permeating though a medium is mathematical identical to the problem of a dielectric material in an electric field (pressure gradient = electrical field, flow of material = electrical flux, pressure = electrical potential).

The Maxwell-model assumes that the dispersed phase consists of uniform spheres and that the pressure gradients within and around each of the particles are not distorted by the presence of other spheres. In case of infinite dilution, the pressure gradients can be calculated exactly [22].

If the continuous and the dispersed phases that make up the membrane are denoted by the subscripts \( c \) and \( d \), and hence the permeabilities of the pure phases \( P_c \) and \( P_d \) and the volume fraction of the dispersed phase \( \phi_d \), the permeability of the mixed matrix membrane is given by:

\[
P_{\text{Maxwell}} = P_c \cdot \frac{P_d + 2 \cdot P_c - 2\phi_d \cdot (P_c - P_d)}{P_d + 2 \cdot P_c + \phi_d \cdot (P_c - P_d)}
\]  \hspace{1cm} (1)

In case of higher concentrations however approximations have to be made. One useful approximation is the mean field approach: the presence of other particles is taken into account by assuming that the material surrounding the embedded particle can be approximated by a homogeneous material of properties given by a weighted average of the properties of the two components. Several procedures have been applied to calculate these average properties: For example it has been assumed that the pressure gradient in the matrix is given by the volume weighted pressure gradients within each of the components (Mawell-Garnett model [23]). It has been assumed that the permeability of the homogeneous material is given by the volume weighted average of the permeabilities of the components (Brügemann model [24]). It has been assumed that a two phase
element in the shape of a spherical or ellipsoidal core and confocal shell is embedded in a homogeneous material, the properties of the homogeneous material given by the condition that its permeability is identical to the permeability of this two phase element (Smith [25]). All these models differ in their predictions, for example the prediction of the Brügemann model is given by [8]:

\[
\left( \frac{P_{\text{Brügemann}}}{P_c} - \frac{P_d}{P_c} \right) \left( \frac{P_{\text{Brügemann}}}{P_c} \right)^{\frac{1}{3}} = (1 - \phi) \left( 1 - \frac{P_d}{P_c} \right)
\]  

(2)

This prediction can not be made explicit for \( P_{\text{Brügemann}} \) by analytical means, but still can be easily computed by numerical iteration. For comparison to the Maxwell model, the prediction according to the Brügemann model has been included into Figure 4 as dotted line.

b) Serial model

If the two phases are forming a stack of two continuous sheets, one placed on top of the other, compounds passing through this stack have to pass both phases and transport is best described by a serial model (in this system there is no distinction between a continuous and a dispersed phase, for simplicity we nevertheless use again \( c \) and \( d \) in the equations below) [5]:

\[
P_{\text{serial}} = \frac{P_c \cdot P_d}{\phi_c \cdot P_d + \phi_d \cdot P_c}
\]

(3)

c) Parallel model

Figure 2: Schematic drawing of mixed matrix membrane described by serial model.

Figure 3: Schematic drawing of mixed matrix membrane describe by parallel model.
If the two phases are confined to domains that all penetrate with vertical walls from the bottom surface of the membrane to the top, the permeability of such a membrane for each compound is given by:

\[ P_{\text{parallel}} = P_c \cdot \phi_c + P_d \cdot \phi_d \]  \hspace{1cm} (4)

Mixed matrix membranes usually comprise a material that is highly selective and highly permeable [10], but has inferior mechanical properties or is available as powder only without a chance to produce a crack-free membrane from it. Thus this powder is embedded in a mechanically stable polymer matrix. It is instructive to have a look at two extreme cases: If the matrix is significantly more permeable than the dispersed phase, the permeating substance shunts the particles. For any substance, the permeability of the membrane is a function of only the permeability of the matrix and the volume fraction of the dispersed phase (but not its permeability).

As a result, the selectivity depends on the matrix only. For example within the Maxwell model one obtains:

\[ \lim_{\frac{P_c}{P_d} \to \infty} (P_{\text{Maxwell}}) = P_c \cdot \frac{1 - \phi_d}{1 + \phi_d / 2} \]  \hspace{1cm} (5)

\[ \rightarrow \text{Selectivity} = \frac{P_{\text{Maxwell}}(\text{Substance 1})}{P_{\text{Maxwell}}(\text{Substance 2})} = \frac{P_c(\text{Substance 1})}{P_c(\text{Substance 2})} \neq f(P_d) \]  \hspace{1cm} (6)

If the particles are significantly more permeable than the matrix, the matrix becomes the mayor obstacle to flow. The permeability of the membrane for any substance is independent on the permeability of the dispersed phase, and thus the selectivity of the whole membrane is independent on the selectivity of the dispersed phase. Again using the Maxwell model as example, one obtains:

\[ \lim_{\frac{P_d}{P_c} \to 0} (P_{\text{Maxwell}}) = P_c \cdot \frac{1 + 2\phi_d}{1 - \phi_d} \]  \hspace{1cm} (7)

A dispersed phase of higher selectivity than the matrix increases the selectivity of the whole membrane only, if the permeability of matrix is matched to the permeability of the dispersed phase. Nevertheless, even if permeabilities are matched, the membrane can not reach the selectivity of the pure dispersed phase (see Figure 4). Very similar predictions are obtained if instead of the Maxwell model (which is of limited accuracy in cases of high volume fraction of dispersed
phase) the more accurate Brügemann model (see dotted line in Figure 4) or other approximations are used. The principal prediction of limited selectivity of mixed transport still prevails even in these more elaborate models.

Figure 4: Selectivity of a mixed matrix membrane made of particles completely embedded in a continuous matrix (composed of 50% vol. dispersed phase, selectivity of the dispersed phase = 2, selectivity of the matrix = 1) as a function of the ratio of the permeabilities of the two phases for the less permeable of the two gases. In case of extremely permeable or impermeable matrix, the membrane has the selectivity of the matrix, if permeabilities are matched, the selectivity is above the selectivity of the matrix, but does not reach the selectivity of the pure dispersed phase.

As already mentioned before, in membranes with serial model architecture there is no distinction between dispersed and continuous phase, but usually it makes sense to call the two phases 'mechanically stable' and 'highly selective', respectively.

In the serial transport, if thin film made from highly selective material would be supported by the a mechanical stable material with much lower permeability; then the selectivity and permeability of the composite membrane would be only in the range of the pure mechanical stable material (Eqn. 8 and Figure 5)

\[
\lim_{\frac{P_c}{P_{d,0}} \to 0} (P_{serial}) = \frac{P_d}{\phi_d P_d + \phi_d}
\]  

(8)
\[
\lim_{\frac{P_c}{P_d} \to \infty} (P_{\text{serial}}) = \frac{P_c}{\phi_c + \phi_d P_c}
\] 

(9)

Figure 5: Selectivity of a mixed matrix membrane in which the two phases are forming continuous sheets in the plane of the membrane (50% vol. dispersed phase, selectivity of the dispersed phase = 2, selectivity of the matrix = 1) as a function of the ratio of the permeabilities of the two phases. In case of extremely permeable matrix, the membrane has the selectivity of the matrix, in case of extremely impermeable matrix, the membrane has the selectivity of the dispersed phase.

To reach the best properties of the membrane with the serial model architecture the mechanically stable phase need to be very permeable (Eqn. 9, Figure 5). The selective phase should be considerable less permeable, however needs to be continuous and absolutely crack-free. Unfortunately zeolites or carbon molecular sieves are very brittle and easily shatter upon bending or stretching, thus the synthesis and especially the non destructive handling of membranes made of thin layers of such materials and a flexible support nowadays is still not feasible.

In case of parallel transport, the limiting cases are always dominated by the more permeable phase (Eqn. 10, 11).
\[ \lim_{\frac{P_c}{P_d} \to \infty} (P_{\text{parallel}}) = P_c \phi_c, \]  

(10)

\[ \lim_{\frac{P_c}{P_d} \to 0} (P_{\text{parallel}}) = P_d \phi_d \]  

(11)

Figure 6: Selectivity of a mixed matrix membrane in which the dispersed phase is embedded in a matrix in such a way that the dispersed phase as well matrix protruded out at both interfaces (50% vol. dispersed phase, selectivity of the dispersed phase = 2, selectivity of the matrix = 1) as a function of the ratio of the permeabilities of the two phases. In case of extremely permeable matrix, the membrane has the selectivity of the matrix, in case of extremely impermeable matrix; the membrane has the selectivity of the dispersed phase.

As can be seen from Figure 6, the selectivity of the membrane now again can be influenced by varying the permeability of the matrix. This time, however, the selectivity is a monotonous function of the permeability of the matrix and approaches the selectivity of the embedded dispersed phase if the matrix is made impermeable to the permeating substances.

The biggest advantage of a membrane allowing parallel transport compared to the serial transport depicted above is the fact that in this latter case the selective phase does not need to be continuous. Thus, a membrane utilising parallel transport can be synthesised and handled with much more ease than membranes utilizing serial transport.
In Figure 7 are shown all the theoretical predictions of permeabilities through composite mixed matrix membranes with different architectures.

![Graph](image)

**Figure 7:** Selectivity of a mixed matrix membranes with different architecture (50% vol. dispersed phase, selectivity of the dispersed phase = 2, selectivity of the matrix = 1) as a function of the ratio of the permeabilities of the two phases.

The theoretical predictions show that the models that offer the best properties of a membrane are serial and parallel model, because of the above mentioned mechanical stability problems associated with a membrane with parallel transport, a membrane utilizing serial transport seems to be the most attractive choice.

In Figure 8 are shown theoretical predictions of the permeability and selectivity of mixed matrix membranes as function of the volume fraction of the dispersed phase. In all these calculations it is assumed that the continuous phase is non selective, but varies in permeability, while the dispersed phase is selective for gas1 by a factor of 4, its properties being identical in each of the diagrams. If the permeability of the non selective 'continuous phase' is much higher than the dispersed phase, a serial arrangement of both phases yields the best performance (Figure 8a and 8b). If permeabilities of the two phases are comparable to each other, selectivity in all three architectures is the same (Figure 8c and 8d). If the permeability of the non selective 'continuous phase' is
much lower than the dispersed phase, a parallel arrangement of both phases yields the best performance (Figure 8e and 8f). Especially instructive if Figure 8f, which predicts that in case of parallel transport a selectivity very close to the one of the dispersed phase can be reached even for volume fractions lower than $\phi = 0.5$. 
Figure 8: Theoretical predictions of the membrane permeability and selectivity as function of volume fraction of the dispersed phase:

a, b) permeability: dispersed phase, gas 1 = 0.5 continuous phase, gas 1 = 10
permeability: dispersed phase, gas 2 = 2 continuous phase, gas 2 = 10

c, d) permeability: dispersed phase, gas 1 = 0.5 continuous phase, gas 1 = 1
permeability: dispersed phase, gas 2 = 2 continuous phase, gas 2 = 1

e, f) permeability: dispersed phase, gas 1 = 0.5 continuous phase, gas 1 = 0.001
permeability: dispersed phase, gas 2 = 2 continuous phase, gas 2 = 0.001
However, until now there are no literature reports that show membranes with parallel model architecture. Most gas separation membranes are synthesized in such way that polymer or monomer solution is mixed with particles of molecular sieves cast onto a solid support for example using a doctor blade and subsequently solidified. All this methods have their limitations. During doctor blading for example the particles may not be bigger than the slit width of the doctor blade and thus can not be made penetrating out of the deposited polymeric layer. If this problem is to be circumvented by using a diluted polymeric solution in the hope that a volume reduction due to evaporation of solvent finally causes the particles to penetrate, one faces the general problem that drying polymer solutions form a skin that is solidified well before the remainder of the solution [26]. Another limitation of all mentioned methods is that the casting is made onto a solid support, thus at least at the bottom side it is not possible that particles protrude out of the polymeric layer.

As already had been shown in chapters 2, 3, 4 and 5 the technique of particle assisted wetting gives the opportunity of protrusion of particles from the both sides of the polymeric layer [27]. Thus, the idea pursued in this chapter is to prepare mixed matrix membrane with parallel model architecture by using the technique of particle assisted wetting, this time however not embedding impermeable inactive silica particles, but highly selective and permeable particles which are embedded in impermeable polymeric matrix (Figure 9).

**Figure 9: Combining the theoretical description of transport in mixed matrix membranes with our experience in membrane preparation using particle assisted wetting into a strategy to obtain separation membranes of improved selectivity.**

As already had been shown in previous chapters of this thesis hydrophobized silica particles and glass beads can assist wetting of the water surface by oil. Pure oil creates lenses on the water surface, and the mixture of the same oil with hydrophobized particles create composite monolayer where particles adhere to the water surface and oil fill the free spaces between them. In these investigations, the silica particles were just used as porogenes and subsequently removed. In the investigation pursued here, however, the embedded particles shall not be removed; instead they shall be used as the selective and permeable phase of a composite membrane with parallel transport. Thus instead of 'dumb' silica we now have to choose an 'intelligent' material, i.e. a material that is highly selective in a technologically important separation process. Three classes of material have been named as such in the recent literature: zeolites, carbon molecular sieves and metal organic frameworks. Out of these three, carbon molecular sieves offer the advantage that they are already comparatively hydrophobic, that they can easily been made in a chemistry lab and that they are inexpensive. Thus, in the project pursued here, it was chosen to use particles made from carbon molecular sieves as selective phase.

Another important point is the matrix which would glue all particles together. William Koros group was very successful to prepare 'mixed matrix' membranes by embedding carbon molecular sieves in a matrix of Matrimid. In that approach carbon molecular sieves made via pyrolysis of a commercially available polyimide – Matrimid 8214 - were embedded in matrix of Matrimid. The membranes were then doctor bladed onto the solid support, then polymer solidified and membranes with completely immersed particles in the matrix were obtained. Their membranes had the structure of a composite of completely embedded particles within a membrane much thicker than the particle size, thus they can be best described by the mixed transport, e.g. Maxwell or Brügemann model. Thus in the context of Koros' work, the choice of Matrimid – which has a permeability comparable to carbon molecular sieves – as matrix was a very good choice.

To obtain membranes with parallel model architecture several strategies are used: (i) to be initially as close as possible to the work of Koros the same materials as in Koros' work is used, but not doctor bladed, but diluted with a good solvent for the Matrimid, spread out on a water surface and then solidified via evaporation of the solvent. (ii) in order to have better control on then preparation process and to reduce the permeability of the matrix, Matrimid is exchanged for
Chapter 6  Mixed matrix membranes for gas separation

non volatile multifunctional methacrylate monomers, that finally give rise to a highly cross-linked polymer. (iii) the process is further optimized by doing the spreading on a Langmuir trough, followed by gentle lateral compression, prior to solidification.

(i) Membranes made out of carbon molecular sieves and Matrimid

The idea is to prepare carbon molecular sieves with the same procedure as already described in William J. Koros' publication [3] and then prepare the same composite membrane as in Koros' work but now on a water surface and in such a way that the particles protrude out of the Matrimid at both sides. For that reason Matrimid 9725, which has the same chemical composition as Matrimid 8214 (used by Koros) is used for the preparation of the carbon molecular sieves: first Matrimid solution in dichloromethane is cast into the Petri dish. After solvent evaporation a polymeric layer is obtained which is then dried under vacuum for complete removal of the solvent. Dried polymeric layer is then pyrolyzed under constant inert gas flow. After pyrolyzation, flat sheet of carbonized Matrimid are obtained. These are milled into a form of powder. Scanning electron microscopy image of this powder of carbon molecular sieves is shown in Figure 10. As can be inferred from the process of preparation and is obvious from the electron microscopy image, the resulting particles now are not spherical, as the silica particles previously used. In principle however, this non spherical shape should not hinder the membrane formation. More crucial however is the non uniform size. If the membrane has a thickness comparable to the average particle diameter, still some particle will not penetrate through.

![Figure 10: SEM image of carbon molecular sieves.](image)

The procedure of mixed matrix membranes preparation where carbon molecular sieves are embedded in the Matrimid matrix is illustrated in Figure 11.
Figure 11: Schematic procedure of membrane preparation via polymer vitrification: a) spreading of particles, b) dense particles layer on the water surface, c) addition of polymer solution, d) solvent evaporation, e) solidified membrane.
As we already learned from the previous chapters it is of advantage to mix the particles and the 'oil' in one solvent and apply them together to the water surface, if the particles are small. In case of larger particles however, it has been more of an advantage to apply first the particles and then, in a second step the 'oil'. Here, the particles are large. Thus, carbon molecular sieves in form of dry powder are carefully applied to the water surface till dense packing of particles is obtained. Then a solution of Matrimid in chloroform is added to the floating particles. In this case, the solidification of polymer is not caused by photopolymerization like it was made in experiments described in previous chapters, but by vitrification of the polymer upon evaporation of the solvent.

The amount of added Matrimid solution chosen in such way that after vitrification, the polymeric layer is thin enough that the particles should protrude out at the top and the bottom of the membrane. The success of the preparation process to some extend depended on the way the solution was manually applied. During addition of polymeric solution at least the first droplets that were added had a large tendency to push the particles aside. Some part of the polymer solution that is deposited form lenses that first were floating between particles on the water surface and finally when solvent evaporates polymeric films are created. Only when the polymer solution is added faster, particles become wetted with this solution instead of being pushed aside and afterwards composite membranes are obtained. An overview image (optical camera) and detail SEM image of a typical membrane are shown in Figure 12.

Figure 12: Composite membrane with embedded carbon molecular sieves in Matrimid; a) image from optical camera; b) SEM image.
As can be seen in Figure 12a the membrane surface is corrugated and in the middle of the polymeric film a hole is obtained. The SEM image (Figure 12a) indicated that the most of particles protrude out in the water phase, while the particles are not visible from the top of the membrane. This indicates that the particles don’t penetrate polymeric layer.

This phenomenon most probable is due the formation of a so called ‘skin layer’. When concentrated polymer solutions are dried, a severe concentration gradient may form at the surface finally giving rise to a highly viscous skin formed by interpenetrating swollen polymer chains [27]. This skin may form even at very initial stages of the evaporation process, well before a significant reduction in volume is to be seen. In the case considered here, when the Matrimid solution is applied onto the water surface, chloroform started to evaporate. At the same time solvent started to diffuse to the water. The evaporation of the solvent is so fast that particles that floated on the water surface don’t have enough time to penetrate both interfaces. Another disadvantage of the skin formation is wrinkling of the membrane surface. In intermediate stages of evaporation, the skin just has a higher concentration and viscosity that the remainder of the polymer solution. Finally, the evaporation of the solvent leads to a shrinking of the membrane laterally as well as in thickness, the higher concentration of the skin is then transformed into a higher volume, thus the skin is subject to a lower degree of shrinking than the remainder of the membrane. This finally causes the formation of wrinkles. The obtained membrane has inhomogeneous, corrugated surface with smaller or bigger holes in it. Membranes obtained with this method are not stable enough to handle them with hand without creation of new cracks.

To improve membrane architecture and stability several parameters are changed: Carbon molecular sieves that are used for the membrane preparation as crude product are very polydisperse. Due to this fact membrane thicknesses differ from place to place. Composite monolayer created from particles with smaller diameter is not as stable as composite monolayer obtained from the particles with bigger diameter. To get smaller variation in the membrane thicknesses carbon molecular sieves are sieved through three sieves with diameter of 50 µm, 75 µm and 95 µm. This gives rise to three fractions of particles with diameters in the range < 50 µm, 50 – 75 µm and 75 – 95 µm. For membranes preparation particles with diameter in the range of 50 – 75 µm are used.

Another important point is to obtain dense packing of particles on the water surface. In previous approach first droplets of polymer solution could not wet the particles but distracted them. In this case particles are deposited onto the surface of water filled Langmuir trough. The
Langmuir trough has two movable barriers which can compress particles and stop their distraction during solution deposition.

Wrinkling of the membrane surface is caused by polymer shrinkage during vitrification. To flatten the membrane surfaces, the shrinkage of the polymer needs to be decreased. From the experiments described in the previous chapters of this thesis it is known that trimethylolpropen trimethacrylate (TMPTMA) stays liquid until the end of solvent evaporation and thus it doesn’t shrink laterally in this stage. In addition the shrinking that occurs during the subsequently initiated photopolymerization is small (approx. 5%) and uniform within the film. After solidification of this monomer usually a flat structure is obtained. Furthermore the result of photopolymerization of this monomer is a highly cross-linked polymer. Thus, if this polymer is used as matrix for the desired membrane one can expect that the matrix would be almost impermeable for gasses. The schematic illustration of the membranes preparation is shown in Figure 13.

Figure 13: The schematic preparation of the mixed matrix membrane on the Langmuir trough with TMPTMA as matrix.
First barriers are placed in the biggest distance that is possible to reach with this kind of Langmuir trough. Then particles are applied onto the water surface in the form of dry powder. Some part of particles that is deposited onto the water surface is submerged under the water surface. Next, the particles layer is compressed with two movable barriers to such extend that the deposited droplet on top of particles could not distract carbon molecular sieves from each other. Then the solution of the TMPTMA and photoinitiator in a solvent is applied onto the top of the particles layer. After solvent evaporation, the monomer is cross-linked. In Figure 14 are shown pictures of the composite membranes.

![Composite membrane with embedded carbon molecular sieves in cross-linked TMPTMA; a) image from optical camera; b) SEM image.](image)

Membranes obtained with this method become flat and more stable than that prepared after Matrimid vitrification. One of the biggest parts of that membrane is shown in Figure 14a. The detail SEM image in Figure 14b shows that particles protruded out at the top and the bottom from the polymeric layer. Compression of the particles by barriers causes dense packing of particles. Cross linking of the monomer with UV light instead of vitrification after solvent evaporation made the membrane surface less corrugated, but the solidified polymeric film became hard and less flexible. Due to that fact, during membrane transportation from the water surface to the solid support a membrane easily breaks into small pieces.

The membranes prepared using TMPTMA were not optimum in mechanical properties, but to some extend brittle, thus the next step is to bring composite membrane higher mechanical stability. For that reason instead of the trifunctional monomer TMPTMA the monomer HEMATMDI is used, the latter has only two methacrylate functionalities per monomer and a larger spacer in
between them. This reduces the cross-linking density and thus the brittleness of the matrix. As previously, the fraction of carbon molecular sieves with diameters in the range of 50 – 75 µm is applied to the surface of the water filled Langmuir trough. Then particles are compressed with two barriers and a solution of HEMATMDI solution is added. The added monomer is then cross-linked with UV light. Obtained polymer should be more flexible due to the longer and more flexible chains obtained after photo-polymerization. The membranes prepared with HAMATMDI are shown in Figure 15.

![Composite membrane with embedded carbon molecular sieves in cross-linked HEMATMDI; a) image from optical camera; b) SEM image.](image)

The mechanical stability of the membranes increased to such an extend that the membrane can be cut with scissors. The SEM picture indicates that particles protruded out at the top and the bottom from the polymeric film (Figure 15b).

Three sorts of the mixed matrix membrane are synthesized. The membranes differ from each other with the thickness. The scanning electron microscopy images are shown in Figure 16.
Figure 16: Side view pictures of the mixed matrix membranes with three different thicknesses: a) approx. 70 µm; b) approx. 90 µm; c) approx. 250 µm.
Because of the pretty big size distribution and irregular shapes of the carbon molecular sieves, the membranes thicknesses are varied with added monomer amount. The first membrane is approximately 70 µm thick, second – 90 µm and third – 250 µm. In each of the membranes the biggest parts of particles protrude more to the water/oil interface than to the air/oil interface. When the amount of added oil decreased, particles started to protrude at the top of the membrane. With higher polymer amount the stability of the membrane increases, but even membranes with the smallest amount of matrix are stable enough to stand the cutting with scissors and can be easily handle with hands.
6.4. Conclusions

The theoretical predictions of the selectivity in the mixed matrix membranes with different architectures have been made. In membranes with parallel transport architecture, the selectivity of the pure high selective phase can be reached. To reach this selectivity, the highly selective material needs to protrude out at the top and the bottom from the matrix. At the same time matrix need to be mechanically stable and impermeable.

Mixed matrix membranes with parallel transport architecture have been prepared. Spreading of the carbon molecular sieves with derivatives of methylmethacrylate onto the water surface yields a composite layer where particles protruded out from the matrix at the top and the bottom. Solidification of the monomer gives rise to the mixed matrix membrane with parallel architecture.

Since now there is no literature report about synthesis of mixed matrix membranes with parallel transport architecture. The concept of particle assisted wetting is a good tool to obtain such membranes.
6.5. Experimental part

6.5.1. Preparation of carbon molecular sieves.

Commercially available polyimide Matrimid 9725 (Huntsman) is dissolved in dichloromethane (technical grade) in such a way that the final concentration of the polymer in the solution was 1% by weight. Then 200 g of the solution is poured into a glass Petri dish with 8 cm in diameter. After 12 hours the polymeric film was formed. The vitrified film was detached from the dish and dried in a vacuum oven by 100°C and 12 mbar over 12 hours. In the next step, the polymer is cut into smaller pieces and then it is placed in the quartz glass tube. The tube is then evacuated and filled with argon. The polymer is then pyrolized in the quartz tube under constant flushing with argon. The temperature program for the tube furnace is shown in Figure 17.

![Temperature program for Matrimid pyrolization.](image)

After pyrolysis, the material had been left in the tube furnace till it cooled down to room temperature.

The pyrolized polymer was milled with a ball mill mixer for 2 minutes. Then particles are sieved in the sieving machine (Retchs) through three sieves with 90, 75 and 50 µm mesh size. The parti-
cles that remained on the sieve with the biggest mesh were milled and then sieved again. This finally gives rise to the three particles fractions: < 50 µm; 50 – 75 µm and 75 – 90 µm.

After sieving each of the carbon molecular sieves fraction is characterized with SEM (NanoNo-vaSEM, Company FEI).

The images of sieved particles are given in Figure 18.

Figure 18: Fraction of particles after sieving a) smaller than 50 µm, b) in the range of 50 – 75µm, c) in the range 75µm – 90µm
6.5.2. Preparation of mixed matrix membranes on the Langmuir trough

Dry particles with size in range of 50-75 µm are spread onto the surface of a water filled Langmuir trough (Riegler & Kierstein, Potsdam) of 14 cm width and 31 cm length, the barriers being fully open at a distance of 29 cm. The particles are spread as dry powder, an excess of particles was blown off with a gentle stream of air. Finally, the particles were dense enough so that a gentle stream of air directed towards the surface in a slant angle would not suffice to rip the particle layer open. Then the barriers were moved inwards till the distance between them is decreased to 7 cm. In the next step, the solution of dimethacrylate 11,14-dioxa-2,9-diazahexadec-16enoic acid,4,4,6,16-tetramethyl-10,15-dioxo-2-[(2-methyl-1-oxo-2-propen-1-yl)oxy]ethylester, (HEMATMDI, PLEX®6661-0/VM015, Röhm, now Evonik Röhm GmbH) and Lucirin TPO-L (BASF) in chloroform (technical grade) is added to the compressed layer of particles. After evaporation of solvent (30 minutes) the composite layer was illuminated with the UV light for 1 hour. The exact compositions of membranes are given in the table 1.

Table 1: The exact compositions of the solution spread onto the layer of carbon molecular sieve particles on the surface of the water filled Langmuir trough.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Membrane 1</th>
<th>Membrane 2</th>
<th>Membrane 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon molecular sieves</td>
<td>1.0784 g</td>
<td>1.1279 g</td>
<td>1.0172 g</td>
</tr>
<tr>
<td>HEMADMTI</td>
<td>0.3098 g</td>
<td>0.3168 g</td>
<td>0.4 g</td>
</tr>
<tr>
<td>Lucirin TPO-L</td>
<td>0.168 g</td>
<td>0.1718 g</td>
<td>0.1971 g</td>
</tr>
<tr>
<td>Chloroform</td>
<td>1.7095 g</td>
<td>1.7497 g</td>
<td>2.0255 g</td>
</tr>
</tbody>
</table>

The solidified membranes are characterized with scanning electron microscopy (NanoNovaSEM, Company FEI) and with thermogravimetry (heating rate 10 K/min, nitrogen atmosphere). In thermogravimetry, the membranes experience a significant weight loss in the temperature range of 30°C -600°C which is in the range of the ceiling temperature of the methacrylate monomer and thus can be associated with the depolymerization and evaporation of the matrix. If one interprets the weight loss as 100% due to complete loss of the matrix, one can deduce the compositions of the solid membranes that are given in the table 2.
Table 2: Compositions of the mixed matrix membranes after solidification.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Membrane 1</th>
<th>Membrane 2</th>
<th>Membrane 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solidified HE-MADMTI [mass percents]</td>
<td>73</td>
<td>77</td>
<td>91</td>
</tr>
<tr>
<td>Caron molecular sieves [mass percents]</td>
<td>27</td>
<td>23</td>
<td>19</td>
</tr>
</tbody>
</table>
6.6. References


Chapter 7

Conclusions

It was shown that mixtures of suitable particles with oil created composite layer on the water surface. Particles protrude at top and at the bottom from the oil layer. Solidification of the oil and removal of the particles give rise to porous membrane. Porous membranes with pores width till 1 µm were prepared.

In the first chapter of this thesis it had been shown that the area of porous membranes can be increased and membranes can be tightly bond to supportive structures like non woven fibrous support (Figure 1). However, membrane surfaces that are bond to the fabric are not flat and this is might lead to cake layer formation during cross flow filtration.

Figure 1: Porous membrane bonded with fibrous support: a) schematic drawing, b) SEM image.
It was concluded that supportive structure need to be flat to get flat membranes that will be attached to its surface. Thus, the next idea was to mount several porous membranes together in such way that they will create hierarchical structure (Figure 2). For that reason it was needed to prepare porous membranes that will be mechanical stable and can be used as new supportive structure. In the chapter 3 it is shown that not only submicroscopic silica particles can be used as porogens for porous membranes preparation but also much bigger glass beads. It is shown that during this membranes preparation gravity need to be taken into account and that etching is not as “simple” as in case of submicroscopic silica particles. In Figure 2b can be see SEM image of porous membrane with 70 µm pore width.

Another important issue was low mechanical stability of porous membranes with pores width smaller that 100nm. Spreading a mixture of two sorts of particles with opposite surface properties with oil onto a water surface gives rise to composite layers in which hydrophobic particles protruded out at the top and less hydrophobic particles at the bottom. Removal of these particles gives rise to the asymmetric membranes with 30 – 50 nm pores.
Chapter 7  Conclusions

As it was introduced in the chapter 5 of this thesis pore functionalization is very important issue in the membrane technology. It was revealed in chapter 5 that etching of silica particles from the membrane that is floating on the water surface is much slower than on the solid support. At intermediate stages of etching the partially etched particles are attached to the pores walls (Figure 4a, b).

To find out how big parts of particles are remaining inside the pores polymeric matrix is pyrolysed. In Figure 5 are shown reaming parts of particles – silica rings.
In the chapter 6 it is shown that it is possible to prepare mechanically stable membranes with embedded irregularly shaped carbon molecular sieves (Figure 7).

Theoretical prediction of gasses permeability and selectivity through membranes with embedded highly permeable and highly selective particles which protrude out at the top and at the bottom from the polymeric matrix showed the highest permeability and selectivity.

Particle assisted wetting method is a new technique for the membranes preparation. Membranes prepared with this technique can be used in ultrafiltration, microfiltration and also in gas separation.
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   „Hierarchically structured porous membranes.” Dawid Marczewski

**Posters:**

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   „The use of particles to shape a membrane – The use of a membrane to shape particles.”
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   DE 10 2006 010 831 0
Selbständigkeitserklärung

Hiermit erkläre ich an Eides statt, die vorliegende Arbeit selbständig und ohne unerlaubte Hilfsmittel durchgeführt zu haben.

Dawid Marczewski

Chemnitz, den 15.12.2008