Chapter 5

Preparation of Rough Surfaces using Teflon® Colloids

In this chapter a novel method for structuring Teflon® colloidal films is described.

5.1 Introduction

Colloidal dispersions are systems in which particles in the micrometer size range are dispersed in a liquid medium. Many products we use in our daily life are colloidal dispersions. Paint, ink, and milk are some examples.

Colloidal particles scatter light if their refractive index differs from that of the dispersing liquid. A light beam travelling through a dispersion is likely to undergo multiple scattering (diffusion). This is easy to spot when a colloidal dispersion is illuminated, even if the dispersion has a transparent appearance. The dispersion affects the light beam in a way which is comparable to the effect of fog in the headlights of a car. This is called the Tyndall effect. Larger colloids show a greater opacity. The
Lorenz-Mie theory describes the scattering of vertically polarised electromagnetic waves by spherical particles. This theory is used in several techniques to determine the size of the dispersed particles.

Colloidal dispersions can destabilise over time. In case of an emulsion, for example milk, the dispersed phase coalesces and forms big oil drops - a phenomenon called coarsening. If the dispersed phase consists of solid particles, van der Waals attractions cause the particles to coalesce and to form aggregates. This aggregate formation reduces the interfacial energy, causing the particles to irreversibly stick together. The resulting aggregates sediment out. If the dispersed particles are less dense than the dispersing liquid, the particles tend to rise to the surface. This phenomenon is usually called “creaming”, in similarity to the formation of cream on milk. If the dispersed particles are denser than the dispersing liquid, the particles tend to sediment. The smaller the dispersed particles, the lower is the influence of gravity. Below a certain particle size, gravity will be overcome by the Brownian motion of the particles.37

To prevent the problem of coalescing colloidal particles, the van der Waals attraction has to be overcome. This can be done by electrostatic or steric stabilisation. In the case of electrostatic stabilisation, the particles have a like electrical charge - and thus repel each other. In the case of steric stabilisation, the particle surface is modified by attaching polymer chains.

Teflon® colloids were obtained in aqueous dispersions which are convenient for dip or flow coating techniques. Usually, the layer of Teflon® colloids is heated above the melting temperature of Teflon® in order to fuse the colloids together, so that they will form a reasonably smooth layer. In this work, however, we made use of the colloidal structure in order to increase the roughness, thereby increasing the hydrophobicity, of the formed Teflon® film.

In order to increase the roughness even further, we mixed the Teflon® colloids with sacrificial colloids. After the film preparation, these colloids are removed and result in a structure with holes. This way, a hierarchical
structure can be prepared, where the colloidal Teflon® structure and the hole structure are superposed.

5.2 Film Formation of Colloidal Particles

The film formation of colloidal particles is a quite common phenomenon in our daily life. Painting is a good example of a colloidal film formation process. When the paint is applied to an object, the solvent evaporates and a layer of colloidal particles remains. If the colloidal particles are monodisperse, interesting ordered structures can form.

The dispersing liquid plays an important role in the film formation process of colloidal particles. At a certain point during the drying process of the film, only a small amount of dispersing liquid remains between the colloidal particles. If the dispersing liquid forms a concave meniscus between the colloidal particles, the surface tension of the liquid - air interface exerts an attractive force between the particles (see Figure 5.1).

![Figure 5.1: The surface tension of the liquid - air interface drags the colloidal particles toward each other.](image)

The highest packing of one layer of similar sized spheres can be achieved by arranging all the spheres in a hexagonal coordination. A
second layer of spheres is best placed into the indentations of the first layer. When adding additional layers, 2 different dense packing structures can be achieved: the face-centered cubic (FCC) structure and the hexagonal close packed (HCP) structure (see Figure 5.2). In a HCP packing the third layer is in register with the first layer. The resulting colloidal crystal exhibits an AB sequence. In a FCC structure, the orientation of the third layer differs from the first 2 layers. The resulting colloidal crystal exhibits an ABC sequence.

The highest obtainable density in a close-packed structure is reached when 74.04 % of the volume is occupied by colloidal particles. The famous scientist Johannes Kepler concluded in 1611 that no higher packing densities are possible. This close packing is also widely used for stacking oranges, and was used for the stacking of canon balls.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{HCP_FCC.png}
\caption{Top view of colloids in a HCP and a FCC structure.}
\end{figure}

In this work a mixture of two different colloidal particles was used, which did not only differ in chemical composition, but also in size. Depending on the size ratio and the volume fraction of the two types of colloids in such a binary system, different ordering phenomena can occur. When considering a binary mixture of colloids with a comparable size, two situations can occur. The first one is that the different sized colloids hinder each other to form a crystal structure, resulting in the
formation of a disordered, glassy state. The other possibility is the for-
formation of a binary crystal.\textsuperscript{38–40} This occurs only for certain particle size
ratios for which a dense packing is possible. The formation of $\text{AB}_2$ - a
structure with alternating hexagonal layers of large and small colloids -
and $\text{AB}_{13}$ - a structure with a cubic arrangement of the large colloids
and a icosahedra of small colloids - are two possible structures that can
form\textsuperscript{41} (see Figure 5.3).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig53.png}
\caption{Top view of colloids in an $\text{AB}_2$ and an $\text{AB}_{13}$ structure.}
\end{figure}

In the case of a binary mixture of colloids with a big size difference,
it is like the large colloids are “swimming” in a sea of small colloids. The
large colloids can form a crystal structure, with the smaller colloids fill-
ing up the interstitial empty space. The presence of small colloids even
enhances the dense packing of the large colloids because of the depletion
attraction. The large colloids have a spherical shell around them into
which the centre of a small colloid cannot penetrate (Figure 5.4a). This
shell is called the depletion zone. When large colloids come in proximity
of each other, their depletion zones overlap. The centre of the small col-
loids cannot enter the overlapping depletion zones (Figure 5.4b). There
is an osmotic pressure difference between the excluded volume for the
small colloids and the surrounding environment. This osmotic pressure
difference pushes the large colloids together (Figure 5.4c).
Figure 5.4: The principle of depletion attraction: a) The depletion zones of the large colloids touch. The small colloids can enter the space between both large colloids. b) The depletion zones of the large colloids start to overlap. The small colloids cannot enter the overlapping depletion zones. c) The large colloids are in contact.

5.3 Sample Preparation

The first step in the sample preparation procedure is the mixing of the Teflon® colloids and the sacrificial colloids. In this work we used Tef-
lon® colloids with a diameter of 200 nm, and a wide range of different sized polystyrene and poly(styrene-co-divinylbenzene) sacrificial colloids. The Teflon® colloids were supplied by DuPont, and the polystyrene and poly(styrene-co-divinylbenzene) colloids were purchased from Sigma-Aldrich. The polystyrene and poly(styrene-co-divinylbenzene) colloids are charge stabilised by sulphate end groups. Divinylbenzene is used as a cross-linker for the bigger polystyrene particles. The feed ratio of styrene : divinylbenzene was 95 : 5. Most of the polystyrene and poly(styrene-co-divinylbenzene) were shipped as 10 %(w/w) solutions, except for the 8 µm colloids which were shipped as a powder. The dispersions are normally used for the calibration of microscopes, the powder consisting out of 8 µm colloids are normally applied as a matting agent for coatings, anti-blocking (sticking of film layers) and lubrication additive for films, and as a filler for ceramics, cosmetics and dental materials. An overview of the colloids used in this work is given in Table 5.1.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Colloid Size (µm)</th>
<th>Supplier</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon® PTFE 30 N</td>
<td>0.2</td>
<td>DuPont</td>
<td>60 % dispersion</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.1</td>
<td>Sigma</td>
<td>10 % dispersion</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.3</td>
<td>Sigma</td>
<td>10 % dispersion</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.46</td>
<td>Sigma</td>
<td>10 % dispersion</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.6</td>
<td>Sigma</td>
<td>10 % dispersion</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.8</td>
<td>Sigma</td>
<td>10 % dispersion</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>1.1</td>
<td>Sigma</td>
<td>10 % dispersion</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>3.0</td>
<td>Sigma</td>
<td>10 % dispersion</td>
</tr>
<tr>
<td>Poly(styrene-co-divinylbenzene)</td>
<td>6.4</td>
<td>Sigma</td>
<td>10 % dispersion</td>
</tr>
<tr>
<td>Poly(styrene-co-divinylbenzene)</td>
<td>8.0</td>
<td>Aldrich</td>
<td>powder</td>
</tr>
<tr>
<td>Poly(styrene-co-divinylbenzene)</td>
<td>25.7</td>
<td>Sigma</td>
<td>10 % dispersion</td>
</tr>
</tbody>
</table>

*Table 5.1: List of chemicals used.*
The Teflon® colloids and the sacrificial colloids were mixed in a volume ratio ($\varphi$) of sacrificial colloids to Teflon® colloids in the range between $\varphi = 0.1$ and $\varphi = 0.8$. Water was added to the mixture to achieve a solid volume fraction of approximately 60%. To achieve such a high solid volume fraction, it was necessary to let the colloids in the 10% dispersions sediment and remove the supernatant water. The mixtures had the appearance of a latex paint. The mixtures were stirred just before they were applied to the substrate.

Glass slides of 2 x 2 cm$^2$ were used as substrates. The mixtures were applied to the substrate using spread-coating. Spread-coating is a technique which uses a blade to apply a solution to a substrate (see Figure 5.5). This is similar to the way butter is spread on a slide of bread. In spread-coating, the blade is fixed and the substrate is moved keeping the spacing between the blade and the substrate constant. A drop of solution is placed onto the substrate in front of the blade. The blade spreads out the solution and a layer with a homogeneous thickness is formed. The thickness can be controlled by changing the distance between the blade and the substrate. The coating speed was approximately 3 cm per second.

After spread-coating, the substrates were placed onto a hotplate set to 120 °C. Subsequently, the temperature was raised to 290 °C to remove the surfactant and to degrade the sacrificial colloids. After about 5 minutes the film colour changed from white to brown. The samples were allowed to cool down to room temperature, and were then washed in chloroform. The film colour changes from brown back to white during this step. What remained were films containing only Teflon® colloids (see Figure 5.6).

The advancing and receding contact angles of a drop of water were measured after the preparation of the films. The surface textures were examined using AFM, SEM, and optical microscopy.
5.4 Results

First, a film of pure Teflon® colloids was made. The advancing water contact angle of a drop of water on that surface was 125°, compared to 115° for a smooth Teflon® film.

Subsequent films were made from mixtures of Teflon® colloids and sacrificial colloids. Visual analysis of the films showed that cracks had formed in most of the films made with polystyrene colloids smaller than 1.1 µm. The other films had a homogeneous appearance without visible cracks.

The surfaces which were made from mixtures with a small size difference of Teflon® colloids and sacrificial colloids showed a disordered
Figure 5.6: Teflon® colloids film treatment: 1) A film of Teflon® colloids mixed with sacrificial colloids after spread coating. 2) The sacrificial colloids are removed by heat degradation and solvation in chloroform. 3) A film containing only Teflon® colloids remains.

(glassy) arrangement of the larger colloids. This was the case for sacrificial colloid sizes of 0.1 µm, 0.3 µm, 0.46 µm and 0.6 µm. Figure 5.7 shows images of films prepared from solutions containing 0.1 µm sacrificial colloids for different values of ϕ.

Figure 5.7: AFM images of films made from solutions containing 0.1 µm sacrificial colloids for a) ϕ = 0.49, b) ϕ = 0.77, and c) ϕ = 0.86.

For the films made from mixtures containing sacrificial colloids with a diameter of 0.8 µm or more, an organised structure forms for values of ϕ approaching 0.74. Figure 5.8 shows films made with 1.1 µm sacrificial...
colloids exhibit an increasingly organised hole structure with increasing values of $\varphi$, up to a critical value of $\varphi$, where the structure collapses.

Figure 5.8: Optical microscopy images of films made from solutions containing 3 $\mu$m sacrificial colloids for a) $\varphi = 0.19$, b) $\varphi = 0.29$, c) $\varphi = 0.53$, d) $\varphi = 0.57$, e) $\varphi = 0.69$, and f) $\varphi = 0.79$.

SEM images were taken of some of the films made from solutions
containing sacrificial colloids with a diameter of 6.4 µm. Figure 5.9 shows images of Teflon® colloids films prepared from mixtures with different values for \( \varphi \).

Figure 5.9: SEM pictures of a) A mixture with an excess of Teflon® colloids, \( \varphi = 0.19 \). b) A mixture with the right amount of Teflon® colloids and sacrificial colloids to form an organised structure, \( \varphi = 0.68 \). c) A mixture with an excess of sacrificial colloids, \( \varphi = 0.85 \). d) A close-up on the structure of the 200 nm Teflon® colloids. The size of the sacrificial colloids is 6.4 µm.

Figure 5.9a shows a film prepared from a \( \varphi = 0.3 \) solution containing 6.4 µm sacrificial colloids. In some areas reasonably organised holes can be seen, separated by homogeneous areas made from Teflon® colloids. In Figure 5.9b an organised pattern of holes can be observed for a film
prepared from a $\varphi = 0.68$ solution containing 6.4 $\mu$m sacrificial colloids. An interesting detail are the small holes inside most of the larger holes. These small holes are via connections to deeper lying cavities. They are the signature of the close packing of the sacrificial colloids. The contact points of the close packed structures gives rise to the via-holes after the removal of the sacrificial colloids. In Figure 5.9c a film prepared from a $\varphi = 0.85$ solution containing 6.4 $\mu$m sacrificial colloids is shown. The collapsed structure is a consequence of the lack of strength of the structure of Teflon® colloids to support itself once the sacrificial colloids were removed.

Figure 5.9d is a magnification of Figure 5.9b. The hierarchical structure of the 200 nm sized Teflon® colloids in addition to the structure of 6.4 $\mu$m wide holes left by sacrificial colloids can be clearly observed. As opposed to the larger colloids, the Teflon® colloids were not arranged on a periodic lattice. This is most likely a consequence of their polydispersity combined with their small size. The edges of the holes in the surface are sharp. It is therefore likely that a drop of water on this surface is in the composite state.

The formed structure differs from previously made self-cleaning surfaces, because this surface consist out of a continuous matrix with depressions, instead of a continuous matrix with protrusions. This makes the design of this structures potentially mechanically more robust, since no vulnerable protrusions are present. The advancing water contact angle for all samples is shown in Figure 5.10.

A clear trend can be seen for the advancing water contact angle as a function of $\varphi$. The water contact angle increases until $\varphi$ reaches a value between $\varphi = 0.5$ and $\varphi = 0.7$. Higher values of $\varphi$ result in a slight decrease in the water contact angle. Despite the fact that there is not an organised structure above a value of $\varphi$ of about 0.74, the surface roughness remains high, accounting for these high values of the water contact angle. For even higher values of $\varphi$, it is not possible to make a continuous film. The water contact angle is lower on films that exhibit
Figure 5.10: The advancing water contact angle of a drop of water on Teflon® colloids films as a function of $\varphi$ for different sacrificial colloid sizes.

a disordered arrangement of the sacrificial colloids. The highest water contact angles are reached with the 8 $\mu$m poly(styrene-co-divinylbenzene) colloids. The advancing contact angle reaches extremely high values, close to 170°.

The contact angle hysteresis is shown in Figure 5.11. The contact angle hysteresis reaches a minimum value between $\varphi = 0.5$ and $\varphi = 0.7$. For these surfaces, there is no significant hysteresis. A drop of water runs off these surfaces at the slightest disturbance. It is likely
that a drop of water on these surfaces is in a composite state due to the fact that the contact angle hysteresis is extremely low, and is decreasing with an increasing value of \( \varphi \). If the drop - substrate interface was in a non-composite state for all values of \( \varphi \), an increase in the contact angle hysteresis as a function of \( \varphi \) is expected, since the surface roughness increases with an increasing value of \( \varphi \). Since the number of holes in the surface increases with \( \varphi \), the solid surface fraction underneath the drop decreases, and is thereby decreasing the contact angle hysteresis.

Figure 5.11: The contact angle hysteresis of a drop of water on Teflon\textsuperscript{®} colloids films as a function of \( \varphi \) for different sacrificial colloids sizes. The error bars are not shown for clarity reasons.
5.5 Mechanical Robustness

As described in Chapter 1, self-cleaning surfaces are vulnerable because of the soft materials used in combination with the surface texture. The design of the structure used in this work consists out of a continuous matrix with depressions instead of protrusions, and is therefore mechanically more robust. The major problem with the surfaces produced with the procedure described in Section 5.3 is the adhesion of the Teflon® PTFE 30 N colloids to the substrate. It is relatively easy to remove the coating from the glass substrate. The DuPont company has a product line called Teflon® Industrial Coatings, which is a system of multiple layers of primer and top coatings that gives a good adhesion to sandblasted metal substrates. We performed experiments using a 459-804 primer coating and a 852-200 top coating. The top coating is very similar to the Teflon® PTFE 30 N aqueous dispersion. The primer coating was spray-coated onto the aluminium substrate with an average roughness, $R_a$, of $1 - 2 \, \mu m$, and cured on a hotplate set to 250 °C for 15 minutes. On top of that, a smooth Teflon® layer was applied by spray-coating and curing on a hotplate set to 410 °C for 5 minutes. Finally, the self-cleaning layer was applied by the procedure described in Section 5.3. The application of a primer coating dramatically improved the adhesion of the coating to the substrate. It is not possible to remove the coating without using excessive force.

Mechanical shear tests at very high pressures were performed in order to get an indication of the mechanical robustness of the coating. A parabolic metal head was pushed against the sample with a constant force, and simultaneously moved across the sample (see Figure 5.12). The damage suffered by the coating was imaged using an ESEM (see Figure 5.13). An applied pressure of 5.1 MPa results in a slight compression of the surface texture (5.13a). This compression is more significant when a pressure of 120 MPa is applied (5.13b). When a pressure of 290 MPa is applied, both the textured top-layer and the underlying Teflon® layer
are peeled off (5.13c), and the aluminium substrate is uncovered when a pressure of 350 MPa is applied.

In Figure 5.14 the contact angle as a function of the applied pressure is shown. The advancing contact angle decreases as a function of the applied pressure until it reaches a value of about 125°. This contact angle still is higher than the contact angle of a smooth Teflon® surface. A high pressure is needed in order to destroy the self-cleaning effect. The contact angle still shows a value that is higher than 140° for a pressure of about 1 MPa. The decrease in receding contact angle is steeper. The surface - liquid interface probably changes from a composite to a non-composite state, what results in a higher contact angle hysteresis.

5.6 Conclusions

Extremely high water contact angles up to about 170° have been achieved by using a patterning technique involving sacrificial colloids dispersed in films made from Teflon® colloids. This is a major increase compared to
a water contact angle of 115° for a smooth Teflon® film, and 125° for a Teflon® film with a colloidal structure. The best results were achieved by using a mixture of Teflon® colloids with 8 µm-sized poly(styrene-co-divinylbenzene) colloids with a value of $\varphi$ between 0.5 and 0.7. These extremely high water contact angles in combination with a negligible contact angle hysteresis makes these films self-cleaning.

Advantages of the self-cleaning surfaces described in this chapter over existing self-cleaning surfaces are that industry grade materials are used and the surface structure forms in a self-organised fashion. Instead of using work-intensive and expensive lithographical techniques, this coat-
Figure 5.14: The advancing and receding contact angle as a function of the applied pressure.

...
φ close to 0.74. Above this value of φ, the structure collapses as a consequence of lack of continuity of the Teflon® colloids to support the structure. Solutions containing sacrificial colloids with a diameter of 0.6 μm or less, form films with a disordered distribution of holes. These films tend to show cracks, especially for films made from solutions with a high value of φ.

SEM images of films made from solutions containing 6.4 μm colloids show a hierarchical structure of 200 nm Teflon® colloids in addition to 6.4 μm wide holes stemming from the sacrificial colloids. The presence of via-holes are an indication for the continuation of the ordered hole structure deeper inside the film. This is potentially useful because a damage of the top layer, reveals the hole structure in a lower lying layer, and thus restores the self-cleaning effect.

The adhesion of the coating was dramatically improved by using a primer coating. When a very high pressure shear force is applied to the coating, the porous surface texture is compressed, resulting in a lower water contact angle and a higher contact angle hysteresis. The surface still has a contact angle higher than 140° for pressures up to 1 MPa. It would be interesting to do some more mechanical tests for pressures up to 1 MPa.