Development of Photo-patterned Composite Structures in Microchannels for Oil Reservoir Research

by

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B.S., Mechanical and Aerospace Engineering, Seoul National University, 2009

Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering at the Massachusetts Institute of Technology

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Abstract

Starting from unstructured glass microchannels, we develop a new method of micro-model fabrication. We build composite structures in a bottom-up manner with ultraviolet projection lithography where the composite structures are composed of tricyclocdecane dimethanol diacrylate and stearic-acid treated calcium carbonate particles. This lithographic method is simple, fast, economical, and versatile compared with previous fabrication methods used for two-phase porous media micromodel experiments. With the micromodels developed in this way, we conduct oil-water two-phase flow experiments around a single cylindrical post with controlled oleophilic/hydrophilic wetting behavior.

Thesis Supervisor: Patrick S. Doyle
Title: Professor of Chemical Engineering
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Contents

1 Introduction 13
  1.1 Micromodels for Oil Reservoir Research 13
  1.2 Limitation of Previous Micromodel Fabrication 14
  1.3 Thesis Overview 15

2 Ultraviolet Projection Lithography 17
  2.1 Free Radical Photopolymerization 17
  2.2 Stop-Flow-Lithography Technique 19
  2.3 Fixed Structures with Surface Activation 20

3 Composite Structure of Tricyclodecane Dimethanol Diacrylate and Calcium Carbonate with Oil-wet Behavior 23
  3.1 Wettability 23
  3.2 Oil-wet Carbonate Reservoirs 27
  3.3 Polymer-Calcium Carbonate Particle Composite 29
    3.3.1 Matrix – Tricyclodecane Dimethanol Diacrylate 29
    3.3.2 Filler – Stearic-acid Treated Calcium Carbonate 30

4 Preliminary Flow Experiment: Oil–Water Flow around a Single Composite Post 35
  4.1 Microfluidic Chip Preparation Procedure 35
  4.2 Composite Post Polymerization and Flow Experiment Procedure 38
    4.2.1 Oil/Water Capturing around Oelophilic/Hydrophilic Posts 41
4.2.2 Water/Oil Repulsion by Hydrophobic/Oleophobic Posts

5 Summary and Future Plans

A Experimental Results Validation with Computational Simulation
List of Figures

1-1 Comparison between microfabrication methods. Figure reproduced from ref. [1]. ........................................... 14

1-2 Schematic of polymeric structure fabrication by UV lithography. ................................................................. 15

2-1 Mechanism of free radical polymerization. Figure reproduced from Paint & Coating Industry magazine, www.pcimag.com. .................................................. 17

2-2 Schematic set-up of ultraviolet projection lithography. This example shows the synthesis of bar-coded, probe-containing particles. Figure reproduced from ref. [6]. ................................................................. 19

2-3 Polymerization reaction inhibition due to the oxygen permeability of PDMS in Stop Flow Lithography. Figure reproduced from ref. [7]. ................................................................. 20

2-4 Surface activation with 3-(trimethoxysilyl)propyl acrylate. ................................................................. 20

2-5 Comparison between the polymerization process in an oxygen permeable PDMS channel and in a surface activated glass channel. .................................................. 21

3-1 Young’s equation for wettability, water-wet and oil-wet surfaces. ................................................................. 24

3-2 The relationship between water contact angle in air, oil contact angle in air, and oil contact angle in water describing hydro-philicity/phobicity and oleo-philicity/phobicity. Figure reproduced from ref. [9]. ................................................................. 25

3-3 Carbonate oil reservoir distribution in the world. Figure reproduced from Schlumberger, www.slb.com. ................................................................. 27

3-4 Wettability distribution among carbonate oil reservoirs. ................................................................. 28

3-5 Goal and approaches to make photo-patternable micromodels with oil reservoir properties. ................................................................. 28
<table>
<thead>
<tr>
<th>Page</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-6</td>
<td>Schematic approach of polymer-CaCO₃ particle composite.</td>
</tr>
<tr>
<td>3-7</td>
<td>Chemical structure of tricyclodecane dimethanol diacrylate.</td>
</tr>
<tr>
<td>3-8</td>
<td>Contact angle measurement of tricyclodecane dimethanol diacrylate.</td>
</tr>
<tr>
<td>3-9</td>
<td>SEM image of calcium carbonate particles. This image is reproduced from Mississippi Lime.</td>
</tr>
<tr>
<td>3-10</td>
<td>The chemical structure of stearic acid and calcium carbonate powder.</td>
</tr>
<tr>
<td>3-11</td>
<td>Micelle adsorption model for stearic acid on the calcium carbonate surface in aqueous medium. Figure reproduced from [13].</td>
</tr>
<tr>
<td>3-12</td>
<td>Water droplet tests on stearic-acid treated and pure-calcium carbonate particles in air.</td>
</tr>
<tr>
<td>3-13</td>
<td>Water contact angles on pure TCDDA and TCDDA + stearic-acid treated calcium carbonate composite surfaces.</td>
</tr>
<tr>
<td>4-1</td>
<td>The fabrication process of PDMS-glass microfluidic chip</td>
</tr>
<tr>
<td>4-2</td>
<td>Delamination issue with PDMS-glass microchannels.</td>
</tr>
<tr>
<td>4-3</td>
<td>Glass(top)-glass(bottom) microfluidic chip used in the experiment (channel widths: 5 x 0.5 mm, 6 x 1.0 mm, 5 x 1.5 mm, channel depths: 0.05 mm, channel lengths: 18 mm).</td>
</tr>
<tr>
<td>4-5</td>
<td>Displacement of decane with the 0.2 psi flow of water around a stearic-acid treated calcium carbonate + tricyclodecane dimethanol diacrylate post.</td>
</tr>
<tr>
<td>4-6</td>
<td>Displacement of decane with the 0.2 psi flow of water around a pure calcium carbonate + tricyclodecane dimethanol diacrylate post.</td>
</tr>
<tr>
<td>4-7</td>
<td>Possible four combinations explain drainage and imbibition processes.</td>
</tr>
<tr>
<td>4-8</td>
<td>Oil capturing by oleophilic post when the decane is displaced by the water flow.</td>
</tr>
<tr>
<td>4-9</td>
<td>Water capturing by hydrophilic post when the water is displaced by the decane flow.</td>
</tr>
</tbody>
</table>
4-10 Water repulsion by oleophilic post when the water is displaced by the

decane flow. .............................................. 42

4-11 Oil repulsion by hydrophilic post when the decane is displaced by the

water flow. .............................................. 42

5-1 Scheme of calcium carbonate in-situ growth. ......................... 44

5-2 Oil/water drainage/imbibition control depends on oleophilicity/hydrophilicity

of the structures. ........................................ 45

A-1 Comparison between a computational and an experimental results: Oil

displacement by water flow with a oleophilic post. ................. 48
Chapter 1

Introduction

1.1 Micromodels for Oil Reservoir Research

It is common practice to use core samples from oil reservoir sites to understand oil-gas-water multiphase flow occurring in an underground oil reservoirs. However, the disadvantages of core-flooding experiments (e.g. opacity, site specificity, ambiguities of experimental parameters) have made it difficult to conduct fundamental experimental investigations of oil reservoirs.

Due to the above limitations of core-flooding experiments, researchers have recently developed synthetic micromodels. Micromodels are generally two dimensional, transparent, and simplified porous microchannels built to visualize and study fluid behavior in porous media. In oil reservoir research, micromodels reflect underground oil reservoir conditions, for example, porosity, permeability, wettability. These reservoir properties are designed and built into micromodels for further understanding of fundamental fluid behavior and interactions among oil-water-rock phases. These micromodel studies in a laboratory environment are required for various real field applications, such as operational practices for oil production, secondary recovery, and reservoir network mapping.
1.2 Limitation of Previous Micromodel Fabrication

As the MEMS (micro-electromechanical systems) technology has developed along with the rapid growth of information technology and semi-conductor industry, more precise and accurate microfabrication techniques have been developed. This microfabrication technology is also adopted in microfluidic research; microfluidic research handles very small amount of reagents to study behavior of fluids in micro-scale. Researchers who are interested in two-phase flow in porous media also have used micro- and macro-scales micromodels in their experiments to investigate fluid behavior for biological, mechanical, and chemical research applications.

There are many microfabrication methods commonly used in oil research; for example, wet etching, plasma etching, and soft lithography [1]. However, most of these fabrication techniques require a great deal of time and effort: cleanroom fabrication, the use of dangerous chemicals, and high unit cost for a single micromodel. Furthermore, these fabrication methods have a disadvantage as regards flexibility; once the design of features or patterns are fabricated, it is nearly impossible to make geometric modifications [2–5].

<table>
<thead>
<tr>
<th>Fabrication method</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Major references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium–Shaw and glass bead</td>
<td>easy to make, choice of wetting properties, cheap to make, no mask needed</td>
<td>fixed or random network geometry cannot be used under dynamic conditions because the lower half of the model cannot be visualized, not suitable for making elongated models due to the manufacturing procedure, fixed wetting properties, cannot be exposed to regular light, requires a clean room to manufacture, mask needed</td>
<td>Cota-Navarro et al. (1997), Cota-Navarro and Federspiel (1999), Chasenower and Calhoun (1992), Thompson et al. (1983, 1990), Cheng et al. (2003)</td>
</tr>
<tr>
<td>Optical lithography</td>
<td>accurate, can reproduce any network pattern, cheap to make</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet etching</td>
<td>relatively easy, choice of wetting properties depending on the chosen material, can reproduce any network pattern</td>
<td>curvature on the walls makes back-light illumination impossible, limited ratio between pore width and depth, mask needed</td>
<td>Wagner and Christie (1983), Johnson (1962), Sauer and Cottam (1994)</td>
</tr>
<tr>
<td>Deep reactive ion etching, laser etching, ion etching</td>
<td>highly accurate, can reproduce any network pattern</td>
<td>limitation on the depth of the model, maximum ratio between width and depth, very expensive</td>
<td>Yoon et al. (2003), Ohara et al. (2010)</td>
</tr>
<tr>
<td>Stereo lithography</td>
<td>three-dimensional structures</td>
<td>low resolution, very expensive</td>
<td>Hull (1986), Michelena et al. (2010)</td>
</tr>
<tr>
<td>Soft lithography</td>
<td>highly accurate, easy to make, can reproduce any network pattern, cheap to make</td>
<td>needs treatment to fix wettability issues, needs clean room to prepare the silicon wafer</td>
<td>Xia and Whitfield (1998), Kim et al. (1996, 1997)</td>
</tr>
</tbody>
</table>

Figure 1-1: Comparison between microfabrication methods. Figure reproduced from ref. [1].
1.3 Thesis Overview

This thesis introduces a new, versatile, and bottom-up microfabrication technique using ultraviolet projection lithography based on the Stop-Flow-Lithography technique developed in the Doyle group, MIT [6]. Top and bottom glass surfaces of microchannels are acrylated, and the polymerized composite structures adhere to the activated top and bottom surfaces. This method has several advantages over previous micromodel fabrication methods. A two-dimensional basic structure unit can be built within milliseconds, so the whole fabrication process of a micromodel with a multitude of geometric structures takes less than an hour. Chapter 3 describes how we can tune the wetting properties of structures with a polymer-calcium carbonate composite approach, either oleophilic or hydrophilic. In Chapter 4, the procedure of micromodel fabrication process is illustrated, and a simplified oil-water flow experiment results are described and analyzed in Chapter 5.

![Figure 1-2: Schematic of polymeric structure fabrication by UV lithography.](image)
Chapter 2

Ultraviolet Projection Lithography

2.1 Free Radical Photopolymerization

Free radical photopolymerization is a successive cross-linking process of free radicals and monomer molecules initiated by ultraviolet irradiation. When a homogeneous mixture of monomers, photoinitiator, and additional functional chemicals is exposed to ultraviolet radiation for a few millisecond or seconds, free radicals are generated by photolysis of light-sensitive photoinitiator molecules. UV radiation cleaves a bond of a photoinitiator molecule, generating highly reactive free radicals. The free radicals cre-

![Figure 2-1: Mechanism of free radical polymerization. Figure reproduced from Paint & Coating Industry magazine, www.pcimag.com.](image-url)
ated from the initiating molecules transfer to the monomer units, attack double bond
groups in monomer molecules, convert monomer molecules to a polymer. Monomer
molecules are successively added to these cross-linking chains, and solid networks of
polymers are created. This photopolymerization process is terminated if two free
radicals join together, a hydrogen atom from one end is abstracted to another, or a
radical abstracts a hydrogen atom from a neighboring molecule.

Photopolymerization is simple, rapid and versatile than other polymerization pro-
cesses, and the application of free radical photopolymerization process can be con-
trolled by exposure time, intensity of ultraviolet light, concentration of photoinitiator,
and selective exposure by using an impenetrable layer.
2.2 Stop-Flow-Lithography Technique

In this work, we utilized the ultraviolet projection lithography technique that has been developed in the Doyle Group, MIT [6]. The Doyle group has developed Stop-Flow-Lithography for high throughput production of ultraviolet cross-linked hydrogels. SFL introduces streams of precursor with a controlled-pressure pump, holds the flow, polymerizes microparticles with specific geometrical features through pre-defined transparent masks, and finally releases microparticles with supplying pressure again. This stop-polymerization-flow sequence is repeated and SFL produces high-resolution microparticles at high-throughput (Figure 2-2). Instead of producing functional microparticles, we utilize this photo-patterning technique to build polymeric structures in initially blank microchannels.
2.3 Fixed Structures with Surface Activation

Figure 2-3: Polymerization reaction inhibition due to the oxygen permeability of PDMS in Stop Flow Lithography. Figure reproduced from ref. [7].

![Diagram of Oxygen Inhibition Layer](image)

Figure 2-4: Surface activation with 3-(trimethoxysilyl)propyl acrylate.

![Diagram of Surface Activation](image)

The only difference between the polymerization process of the previous Stop-Flow-Lithography and the process of the building fixed structures is whether polymerized particles are floating particles, or fixed structures in microchannels. During the SFL process, polymerized particles are not bound to the top and bottom surfaces due to the oxygen permeability of PDMS(Polydimethylsiloxane). A thin oxygen layer prevents the polymerization of precursor solutions near top and bottom surfaces by forming inhibition layers [7].

Since we want to build desired structures in microchannels with a bottom-up
approach, it is required to modify top and bottom surfaces chemistry to hold the polymerized structures in microchannels. We adapt a surface activation procedure as previously done by Srinivas et al. as follows for fixed PEG-DA (Poly(ethylene glycol) diacrylate) hydrogel posts in bioassays [8]. First a glass(top)-glass(bottom) channel is filled with 1M sodium hydroxide aqueous for 1 hour. After thoroughly rinsing the microchannel with ethanol and water, the channel is filled with 3-(trimethoxysilyl)propyl acrylate for 5 min. The microchannel is thoroughly rinsed with ethanol and water again, and cured at 80°C for 15 minutes for sufficient reaction. Later, when ultraviolet polymerization reaction occurs, the top and bottom glass surfaces modified with acrylate functional group promotes polymer structure fixation on the surfaces (Figure 2-4).

Figure 2-5: Comparison between the polymerization process in an oxygen permeable PDMS channel and in a surface activated glass channel.
Chapter 3

Composite Structure of Tricyclodecane Dimethanol Diacrylate and Calcium Carbonate with Oil-wet Behavior

3.1 Wettability

Wettability describes the spreading preference of liquids on a solid substrate. For the same amount of liquid, the more a liquid drop tends to spread out on a surface, the more liquid and solid molecules like each other and we consider that the wettability of the liquid on the solid surface is good. The wettability is conventionally measured by contact angle. This contact angle is formed by the balance of adhesion force (force between liquid and solid surface) and cohesion force (the intermolecular force of liquid). This force balance is expressed by Young’s equation.

At pore level fluid displacements in oil reservoirs, oil interacts with the other phases, gas, brine, water and surfactants. When these transport phenomena occur in porous reservoirs, the wettability and geometrical features of oil reservoirs are important factors and have to be considered. In this experimental study, we are interested
in oil-water flows around geometrical structures with a tuned wetting property. As mentioned above, since the wettability is a relative preference of a solid surface, we need to define the wetting property of oil-wet (oleophilic) and water-wet (hydrophilic) depends on the configuration of water contact angle in oil (Figure 3-1). The relationship between interfacial tensions and the contact angle configuration is described by Young’s equation. (Eqn. 3.1)

\[
\gamma_{os} - \gamma_{ws} = \gamma_{wo} \cos \theta_{wo},
\]

where

- \(\gamma_{os}\) = the interfacial tension between the oil and solid phases,
- \(\gamma_{ws}\) = the interfacial tension between the water and solid phases,
- \(\gamma_{wo}\) = the interfacial tension between the oil and water

There are no clear boundaries for the distinction of water-wet, intermediate-wet, or oil-wet. However, generally a surface is considered water-wet when a water contact angle in oil is less than 75°, intermediate-wet when the contact angle is 75° \(\sim\) 105°, and oil-wet when the contact angle is greater than 105°.
Figure 3-2: The relationship between water contact angle in air, oil contact angle in air, and oil contact angle in water describing hydrophilicity/phobicity and oleophilicity/phobicity. Figure reproduced from ref. [9].
The water contact angle in oil can be also described by the relationship between water contact angle in air (hydrophilic/hydrophobic) and oil contact angle in air (oleophilic/oleophobic) as derived by Jung et al. [9]:

\[ \cos \theta_{wo} = \frac{\gamma_{wa} \cos \theta_{wa} - \gamma_{oa} \cos \theta_{oa}}{\gamma_{wo}} \]  

(3.2)

where

- \( \cos \theta_{wo} \) = water contact angle in oil,
- \( \cos \theta_{wa} \) = water contact angle in air,
- \( \cos \theta_{oa} \) = oil contact angle in air,
- \( \gamma_{wa} \) = the surface tension of water,
- \( \gamma_{oa} \) = the surface tension of oil,
- \( \gamma_{wo} \) = the interfacial tension between the oil and water

In this work, since we are mainly interested in a water-oil two-phase flow in porous media, we measured water contact angle in oil for relevant surfaces rather than measuring oil contact angle in air and water contact angle in air separately.
3.2 Oil-wet Carbonate Reservoirs

It is estimated that more than 60% of the world’s oil and 40% of the world’s gas reserves are held in carbonate reservoirs. For example, the Middle East is dominated by carbonate rocks, with around 70% of oil and 90% of gas reserves held within these reservoirs (Figure 3-3). When it comes to carbonate reservoirs, even though their main component, calcite, inherently shows water-wet behavior, the surface wetting property of carbonate oil reservoir rocks are known to be mostly oil-wet. Treiber et al. investigated 50 samples and showed that only 8% of the carbonate reservoir rocks were water-wet, 8% intermediate-wet, and 84% oil-wet (Figure 3-4) [10]. They explained that this is because absorbed organic components from the crude oil change most of the carbonate rocks from water-wet to oil-wet.

Figure 3-3: Carbonate oil reservoir distribution in the world.
Figure reproduced from Schlumberger, www.slb.com.

For the above reason, oil reservoir research with micromodels takes wettability as an important factor [11]. We attempted to make structures containing real calcium carbonate particles instead of polymeric or glass structures in microfluidic channels. In order to make structures with calcium carbonate we took two approaches: (1)
Figure 3-4: Wettability distribution among carbonate oil reservoirs.

an in-situ calcium carbonate growth method using water absorptive hydrogel posts, and (2) a polymeric composite method. By using a photo-crosslinkable polymer as a binding material at minimum concentration, we can make calcium carbonate + tricyclocdecane dimethanol diacrylate composite structures. In this thesis, we concentrate on describing the polymer-CaCO$_3$ composite approach. (Figure 3-5).

Figure 3-5: Goal and approaches to make photo-patternable micromodels with oil reservoir properties.
3.3 Polymer-Calcium Carbonate Particle Composite

The aim of this research is to make a photo-pattered geometry in microfluidic channels with designed wetting behavior. The approach 1–B is able to tune the wetting property of polymer-CaCO₃ composite structures by adding hydrophilic or oleophilic calcium carbonate filler to the polymer matrix.

![Figure 3-6: Schematic approach of polymer-CaCO₃ particle composite.](image)

The matrix material that we use in this work has a neutral wetting property and the added CaCO₃ particles are hydrophilic (pure CaCO₃) or oleophilic (stearic-acid treated CaCO₃) particles. In other words, we tune the wetting property with hydrophilic/oleophilic filler materials. Figure 3-6 shows the scheme of this approach.

3.3.1 Matrix – Tricyclodecane Dimethanol Diacrylate

![Figure 3-7: Chemical structure of tricyclodecane dimethanol diacrylate.](image)

We use tricyclodecane dimethanol diacrylate (TCDDA) as our matrix, binding material. TCDDA exhibits desirable features as a matrix material in this study such
as, low shrinkage rate, non-porosity, low reactivity against solvents, good ultraviolet transmission, fast polymerization, and intermediate wettability.

We have also tested PUA (polyurethane acrylate) and NOA81 (Norland Optical Adhesive, thiolene resin) as candidates, but both PUA and NOA81 show hydrophilic properties. Because we want to tune the wetting property of the composite structures with respect to the wetting properties of the filler materials we use, in this case oleophilic/hydrophilic calcium carbonate particles, we need a polymeric matrix which has an intermediate wetting property. TCDDA has an intermediate wetting property, and it is also good for mixing with either the stearic-acid treated calcium carbonate (oleophilic) or the pure calcium carbonate (hydrophilic). The low viscosity and the refractive index of TCDDA are suitable for this work.

![Contact Angle Measurement](image)

Figure 3-8: Contact angle measurement of tricyclodecane dimethanol diacrylate.

We first investigated the wetting property of TCDDA by measuring water contact angle in oil. The water contact angle on flat TCDDA substrates submerged in decane is $\theta_a = 108^\circ$ (advancing contact angle). Since the value of advancing contact angle is generally accepted as an equilibrium contact angle, we consider the wetting property of the matrix to be relatively intermediate. Therefore, if a final polymerized composite material shows oil-wet or water-wet characteristics, we can say that it is due to the wetting property of mixed oleophilic or hydrophilic filler materials since the matrix material has an intermediate wetting property of intermediate.

### 3.3.2 Filler – Stearic-acid Treated Calcium Carbonate

Calcium carbonate is inherently a super-hydrophilic material, but in this work we have to modify the surface property of calcium carbonate from super-hydrophilic to
oelophilic to mimic carbonate rocks in oil reservoirs. Fatty acids are commonly used surfactants to modify the surface property of calcium carbonate, and Gilbert et al. found that stearic acid is the most effective material among different kinds of fatty acids [12]. We followed a stearic-acid coating method from a previous work [13], and the calcium carbonate particles are supplied by Mississippi Lime in the form of dry powder. The particles are produced by precipitation, the mean particle size is 1.25 μm, and the type of crystal is acicular aragonite.

![Figure 3-9: SEM image of calcium carbonate particles. This image is reproduced from Mississippi Lime.](image)

Calcium carbonate particles are coated with stearic acid in acetone, which is a good solvent of stearic acid. The calcium carbonate particles are first fully wetted in acetone. Then stearic acid in acetone (5 wt%) is added to the calcium carbonate suspension and kept in a reaction vessel. The suspension is then agitated for 4 hours at 80°C by a magnetic stirrer.

![Figure 3-10: The chemical structure of stearic acid and calcium carbonate powder.](image)
Shi et al. [13] investigated and proposed the adsorption model of stearic acid on the calcium carbonate surfaces. They described the adsorption process of stearic acid in two steps. First, the chemisorbed monolayer of stearic acid is formed on calcium carbonate surfaces, and hydrophilic head of stearate ion towards calcium carbonate surface. Then multilayers of stearate micelles physically absorbed is followed by tail-to-tail arrangements.

Figures 3-12 and 3-13 show how we check the result of stearic-acid treatment on calcium carbonate particles. We prepare flat surfaces with stearic-acid treated and non-treated calcium carbonate particles and first check a water contact angle in air to confirm the surface modification. Water drops bead up on stearic-acid treated
calcium carbonate particles while water is soaked by pure calcium carbonate particles. However, it is important to note that water repellency in air doesn’t necessarily mean the surface prefers oil over water. However with the water droplet test, we can quickly verify that the surface property is changed by the treatment.

![Diagram](image)

Figure 3-13: Water contact angles on pure TCDDA and TCDDA + stearic-acid treated calcium carbonate composite surfaces.

We also check water contact angles in the oil phase to see whether we can use this stearic-acid treated calcium carbonate to tune the surface property of the composite material 3-13. By mixing hydrophilic or oleophilic calcium carbonate to the TCDDA precursor solution, we want to cover the whole range of wetting properties from water-like to oil-like to achieve the universality of this composite method. The test shows that in the presence of water and oil phases, compared with pure TCDDA surface, the composite surface of TCDDA + stearic-acid treated calcium carbonate particles shows a higher water contact angle, and this means the oleophilicity is increased by adding stearic-acid treated calcium carbonate to TCDDA. However, here we also need to check whether this high contact angle is because of the particles exposed on the surface or because of the roughness increase due to particles under sub-surface. If the calcium carbonate particles are exposed and the wetting property of surface changes due to the dominant coverage of particles on the surface, the high water contact angle is what we wanted. If the calcium carbonate particles under the surface change the roughness of surface, that can also increase the oleophilicity of surface. The
roughness increase makes hydrophilic surfaces more hydrophilic, oleophilic surfaces more oleophilic. We are working on this issue to properly characterize the wetting properties of composite surfaces.
Chapter 4

Preliminary Flow Experiment: Oil–Water Flow around a Single Composite Post

4.1 Microfluidic Chip Preparation Procedure

Figure 4-1: The fabrication process of PDMS-glass microfluidic chip
Initially we used microchannels fabricated from glass-PDMS (Polydimethylsiloxane). Top parts of microchannels were made of PDMS blocks that have a straight channel using soft lithography. Thoroughly washed top PDMS parts and glass slides (0.2 mm of thickness) were plasma treated for 1 min, bonded together, and baked for 15 min at 80 °C for firm adhesion. However, after building the polymeric posts in glass-PDMS microchannels, we found that top surface of the polymerized posts were not fully bonded to the PDMS surface during flow experiments. This delamination issue could complicate flow experiment analysis. We suspect the gap between the polymeric post and PDMS surface is because of the difference of acrylation density on glass and PDMS surfaces; PDMS has less dense acrylate sites on its surface than that of glass surface.

![Delamination issue with PDMS-glass microchannels.](image)

For the above reason, we changed our microchannels from PDMS-glass microchips to all glass microfluidic chips (Hilgenberg GmbH, Germany). For surface activation, we follow the procedure previously described by Srinivas et al. [8]. First, the straight channel is filled with 1M sodium hydroxide (NaOH) solution for 1 hour. The channel is rinsed with ethanol, deionized water, and dried with argon gas. The cleaned channel is then filled with 3-(trimethoxysilyl)propyl acrylate for 5 min. It is rinsed thoroughly
with ethanol and water, and cured at 80°C for 15 minutes to ensure fixation of the TCDDA + calcium carbonate post to the top and bottom glass surfaces during ultraviolet projection polymerization.

Once a surface-activated glass-glass channel is ready, the channel is filled with the precursor solution of tricyclodecane dimethanol diacrylate-calcium carbonate composite. A transparent mask with a desired geometrical feature is placed in the field-stop of inverted microscope and the precursor solution is polymerized with a controlled UV exposure (optimized condition of UV intensity and exposure time). The channel is washed thoroughly with an ethanol. Subsequent flow experiments are conducted by filling the channel with decane(oil phase) and the displacement of oil-phase with water flooding at constant pressure supply, or with reversed sequence.
4.2 Composite Post Polymerization and Flow Experiment Procedure

With proper ratios between calcium carbonate particles, tricyclodecane dimethanol diacrylate and photoinitiator (Darocur 1173), oleophilic and hydrophilic composite posts are built with stearic-acid treated calcium carbonate and pure calcium carbonate, respectively. Thoroughly mixed composite precursor is injected in the activated glass-glass channel using syringes and UV-polymerization is done on the stage of an inverted microscope (Zeiss Axio Observer A1). A photomask with desired geometrical shapes is inserted in the field stop of the microscope, the microchannel is placed and aligned properly. UV exposure time is controlled with a LED light source on/off by LabView program.

![Figure 4-4: Micromodel experiment steps: 1. Polymerization by UV lithography, 2. Washing uncured precursor, 3. Filling decane, and 4. Flowing water.](image)

Figures on the next page show the oil displacement flow by water around oleophilic post (Fig. 4-5) and hydrophilic post (Fig. 4-6) with time. Since the oleophilic post prefers oil rather than water, the oleophilic post forms a thin oil-film layer between the post and water. The oleophilic post is finally encapsulated by an oil-ring while the hydrophilic post touches the entering water phase and leaves only the small amount of oil phase at the posterior area.
Figure 4-5: Displacement of decane with the 0.2 psi flow of water around a stearic-acid treated calcium carbonate + tricyclodecane dimethanol diacrylate post.

Figure 4-6: Displacement of decane with the 0.2 psi flow of water around a pure calcium carbonate + tricyclodecane dimethanol diacrylate post.
We can make a map of four possible combinations with two posts (oleophilic/hydrophilic) and two flow sequences (oil-water/water-oil flows). These four combinations can be used to demonstrate or explain the phenomenon of drainage, when a non-wetting entering fluid displaces a wetting fluid; and the imbibition, when a wetting fluid displaces a non-wetting fluid.

Figure 4-7: Possible four combinations explain drainage and imbibition processes.
4.2.1 Oil/Water Capturing around Oelophilic/Hydrophilic Posts

Figures 4-8 and 4-9 show how oil/water is captured around oleophilic/hydrophilic posts with time when the posts prefer the displaced phase to displacing phase.

Figure 4-8: Oil capturing by oleophilic post when the decane is displaced by the water flow.

Figure 4-9: Water capturing by hydrophilic post when the water is displaced by the decane flow.
4.2.2 Water/Oil Repulsion by Hydrophobic/Oleophobic Posts

For the same oleophilic/hydrophilic posts used in previous section we do reverse flow sequences, respectively. Figures 4-10 and 4-11 show how water/oil is repelled by oleophilic/hydrophilic posts with time when the posts prefer the displacing phase to displaced phase.

![Figure 4-10: Water repulsion by oleophilic post when the water is displaced by the decane flow.](image1)

![Figure 4-11: Oil repulsion by hydrophilic post when the decane is displaced by the water flow.](image2)
Chapter 5

Summary and Future Plans

During my Master's work in Mechanical Engineering at MIT, I have conducted experimental microfluidic research to build robust and reproducible micromodels for oil reservoir study. The idea and procedure of a bottom-up fabrication method for easier building and modification of geometrical structures in micromodels are described. Using controlled ultraviolet light and transparency masks that have pre-defined geometries, it is possible to build cross-linked polymeric structures in blank microchannels. This versatile photo-patterning technique can easily produce multiple and various patterns within blank standard microfluidic chips, which can save considerable time and fabrication effort. The potential application of my research is developing microfluidic platforms that can mimic underground oil reservoir environments under laboratory conditions.

I intend to improve and complete this experimental research during my doctoral work along with to study theoretical modeling of microfluidic systems. Once I set up this photo-definable, wetting-controllable microfluidic system and conduct flow experiments properly, I can propose physical interpretations of experimental results with respect to wettability, competition of forces, hydrodynamic force by shear flow and surface adhesion force by chemical interactions.

I intend to conduct experiments with various kinds of oil-water nanoemulsions for enhanced oil recovery research and functional smart particles for oil reservoir information within micromodels fabricated by the method introduced in this thesis.
As introduced in this thesis, we plan to develop the in-situ calcium carbonate growth method too. This growth method is different from the composite method and we expect to see different features and mechanisms of calcium carbonate growth in microfluidic channels. We are already doing preliminary experiments of this growth method experiments (Figure 5-1).

With completing the map of wetting properties, we are planning to do flow experiments with a single post or multiple posts and to do the dimensional analysis of flow patterns for further understanding of the oil-water two-phase flow (Eqn. 5.1).

\[
A = f(W, D, \rho_{\text{water}}, \rho_{\text{oil}}, \mu_{\text{water}}, \mu_{\text{oil}}, \gamma_{\text{water-oil}}, \theta_{\text{post receding}}, \theta_{\text{channel wall receding}}) \tag{5.1}
\]

- \(A\) = the captured area of oil or water (two-dimensional assumption)
- \(W\) = the width of the microchannel
- \(D\) = the diameter of the post
- \(\rho_{\text{water}}\) = the density of water
- \(\rho_{\text{oil}}\) = the density of oil
- \(\mu_{\text{water}}\) = the viscosity of water
- \(\mu_{\text{oil}}\) = the viscosity of oil
- \(\gamma_{\text{water-oil}}\) = the interfacial tension of water and oil
- \(\theta_{\text{post receding}}\) = the receding contact angle of the post
- \(\theta_{\text{channel wall receding}}\) = the receding contact angle of the channel wall
Figure 5-2: Oil/water drainage/imbibition control depends on oleophilicity/hydrophilicity of the structures.
Appendix A

Experimental Results Validation with Computational Simulation

Thanks to help of Ankur Gupta of the Doyle Group, Chemical Engineering, MIT, we were able to validate our experimental results with computational simulation results. Computational simulation was done with an open source CFD software, OpenFOAM (Open source Field Operation And Manipulation). With the same properties of experiments, for example fluid properties of decane and water, geometric features of cylindrical post and channel width, flow velocity condition, and most importantly wetting property of the post are applied to the computational simulation. We see a decent agreement between experiments and simulation results. This computational simulation will help us to predict, validate and support micromodel experiments and hence it would save time and efforts.
Figure A-1: Comparison between a computational and an experimental results: Oil displacement by water flow with a oleophilic post.
Bibliography


