### RHEOLOGY AND DYNAMICS OF CAPILLARY FOAMS AND THEIR APPLICATIONS TO ENHANCED OIL RECOVERY

A Dissertation Presented to The Academic Faculty

by

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# RHEOLOGY AND DYNAMICS OF CAPILLARY FOAMS AND THEIR APPLICATIONS TO ENHANCED OIL RECOVERY

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To the Almighty God, for the Grace and Mercy to complete this work

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### LIST OF SYMBOLS AND ABBREVIATIONS

- $\phi_q$  Gas volume fraction or foam quality
- $\phi_p$  Particle volume fraction
- $\phi_{rcp}$  Random close packing fraction
  - $\gamma$  Strain amplitude
- $\Gamma_{aw}$  Surface tension
  - $\Gamma$  Interfacial tension
  - $\dot{\gamma}$  Strain rate or apparent strain rate
  - $\dot{v}$  Volumetric flow rate
  - $\theta$  Three-phase contact angle
  - $R_p$  Particle radius
  - K Boltzmann constant
  - T Temperature
- $\Delta E$  Adsorption energy
  - *l* Characteristic bubble size
  - L Characteristic instrument scale or length
  - $\sigma$  Shear stress
  - $\omega$  Frequency
- G' Storage or elastic modulus
- G" Viscous or loss modulus
- G<sub>0</sub> Plateau modulus
- G Shear elastic modulus
- R Bubble radius

- $\tau_c$  Characteristic relaxation time
- $\tau$  Decay time
- $\sigma_c$  Critical stress
- $\sigma_v$  Yield stress
- $\eta$  Viscosity
- *ρ* Oil-particle volume ratio
- $V_0$  Initial foam volume
- $V_{\infty}$  Final foam volume
- V Foam volume
- $\varepsilon$  Liquid volume fraction
- $R_0$  Initial bubble radius
- $\Delta P$  Differential pressure
  - t Time
  - $\hat{t}$  Dimensionless time
- $t_f$  Final time
- *k* Absolute permeability
- A Cross-sectional Area
- $R_{o/I}$  Ratio of bubbles exiting versus entering
- O/W Oil-in-water emulsion
- W/O Water-in-oil emulsion
  - Ca Capillary number
  - CF Capillary foam
- CGF Colloidal gel foam
  - CS Capillary suspension

- CSR Controlled strain rate
- CSS Controlled shear stress
- EOR Enhanced oil recovery
  - FS Frequency sweep
- HMDS Hexamethyldisilazane
  - ID Inner diameter
  - OD Outer diameter
- PDMS Polydimethylsiloxane
  - PE Polyethylene
  - PF Pickering foam
  - PP Parallel plate
- PTFE Polytetrafluoroethylene
  - PV Pore volume
- PVC Polyvinyl chloride
  - SF Surfactant foam
- TMPTMA Trimethylolpropane trimethacrylate

#### SUMMARY

Aqueous foams, gas dispersions in water, are ubiquitous; they are found in products and processes such as cosmetics (shampoos, shaving cream), food and drinks (whipped cream, beer), firefighting, froth floatation, enhanced oil recovery, etc. In many of these applications, foams provide a variety of functional and sensory benefits because of their elastic and viscous rheological properties. In enhanced oil recovery (EOR) operations, for example, foams can provide uniform displacement of oil that is trapped in underground reservoirs by blocking large pores, reducing gas mobility, and preventing viscous fingering.

Foams, though useful, are unstable systems that phase separate over time. The effectiveness of traditional surfactant foams (SFs) in EOR operations is further limited on contact with oil, which is a defoaming agent that destabilizes the foam structure. Recently, a new class of aqueous foams known as capillary foams (CFs) was discovered to be stabilized by the synergistic action of colloidal particles and a small amount of oil. The gas bubbles in CFs are coated by a thin film of oil and embedded in a gel network of oil-bridged particles. CFs have been observed to remain stable for months and are promising for applications like EOR where its oil-tolerance, long lifespan, and rheological properties could prove beneficial. The unique architecture of CFs is however expected to affect foam rheology and induce properties differing from those of traditional foams. Therefore, the goal of this thesis is to investigate the rheological properties of capillary foams, understand how the oil-particle network influences foam dynamics and determine the feasibility of using capillary foams in enhanced oil recovery operations.

The rheological properties of CFs were thoroughly probed in steady shear and oscillatory measurements carried out on a rheometer. Fundamental analysis on CF rheology data showed solid and liquid regimes with a finite yield stress separating both regimes. The observed CFs properties, elasticity, relaxation time, and yield stress, were compared to properties reported for other soft materials and were found to be in the range of similar properties for traditional aqueous foams with gas volume fractions.

The effects of constituent variations on the structure and properties of CFs were established by combining observations from foaming, microscopy, and rheology measurements. The findings here revealed that the particle wettability not only determines the type of gel network formed, but also influences the prevalence of oil droplets included within the foam. Data also revealed that the stability and rheology of CFs are mainly a function of the particle volume fraction whereas the foamability and observed microstructure are sensitive also to the oil-to-particle ratio.

Following the fundamental understanding of CF rheology, the dynamics of CFs flowing through a tube were explored to determine the stability of CFs under shear and to understand the effect of shear on the CF structure. The results of this study showed that CF stability is dependent on the imposed flow rate and that low flow rates negatively impact the CF structure through phase separation during unsteady flow. It was further observed that strengthening the gel-network, by increasing the particle concentration, can mitigate structural damage to CFs at low flows because the oil-particle network better protects the embedded bubbles.

Finally, this thesis focused on applying CFs to EOR by studying the bubble-particle dynamics of CFs in a micromodel. Porous media flow studies indicate events that occur in underground pores and provide insights that improve oil displacements from underground wells. Three stages in CF flow are highlighted and discussed in relation to foam mobilization and pore clogging by particles and bubbles. The major bubble generation and destruction mechanisms of lamella division, snap off, and coalescence were discovered in microflows of CF. CFs are shown to displace crude oil from the micromodel and achieve a higher sweep efficiency than when water alone is used as the displacing fluid. However, when oil displacement in CFs and SFs are compared, SFs are found to require significantly less foam volume, than CFs, to high sweep efficiency in porous environments.

The fundamental studies in this work provide an understanding of the underlying physics that govern CF rheology and dynamics, as well as methods for tuning CF rheology for various applications in products and processes. The results of the micromodel studies indicate that the CF flooding, though promising for EOR, needs to be optimized to achieve effective oil displacement from underground reservoirs.

#### CHAPTER 1. INTRODUCTION

#### 1.1 Aqueous Foams

Foams are colloidal systems of gas bubbles suspended within a continuous liquid phase. The morphology of a foam is characterized by the volume fraction of gas ( $\phi_g$ ) present in the foam. At high gas volume fractions ( $\phi_g > 0.7$ ), the foam is referred to as a dry foam; as shown in Figure 1-1, the continuous liquid in a dry foam exists in thin films between polyhedral shaped bubbles and in plateau borders where three bubble films meet. On the other hand, when  $\phi_g < 0.7$ , spherical bubbles are well dispersed within the liquid phase in what is described as a "wet foam". Bubbles in foams can be monodisperse or polydisperse depending on the stabilization mechanism, the method of preparation, type of gas and liquid present, etc.



Figure 1-1 Vertical profile of a foam sample showing its structure at different gas volume fractions ( $\phi_g$ ). (b) Expanded bubble shapes at high  $\phi_g$  (top) and low  $\phi_g$  (bottom). Adapted from US NAVAIR 2012.<sup>1</sup>

Foam formation involves generating a gas-liquid interface; this process is not spontaneous and requires energy input using mechanical or chemical techniques.<sup>2</sup> Once created, foams are thermodynamically unstable because the high energy ( $\Gamma_{aw}$ ) associated with the gas and liquid interface constitutes a driving force for decreasing the overall surface area in foams. However, foams can be kinetically stabilized through the adsorption of surfactant molecules or particles at the gas-liquid interface as shown in Figure 1-2. Surfactant molecules slow down the thinning and bursting of foam films through (i) Marangoni flows that counter surface tension gradients, (ii) steric and electrostatic repulsions that repel foam films, and (iii) resistance to ripening and drainage.<sup>3</sup>



Figure 1-2 (a) Schematic of the air-water interface of a surfactant stabilized foam.<sup>4</sup> (b) Micrograph of spherical shaped surfactant bubbles; reprinted from ref 5, Copyright 2007, with permission from Elsevier.<sup>5</sup> (c) Schematic of the air-water interface of a particle stabilized bubble; adapted by permission from ref 6, Copyright 2006.<sup>6</sup> (d) Confocal micrograph of foam stabilized by polystyrene latex particles; reprinted with permission from ref 7. Copyright 2006 American Chemical Society.<sup>7</sup>

Colloidal particles adsorbed at the gas-liquid interface can form a dense layer that limits coarsening and coalescence and reduces drainage by increasing the viscosity of the continuous liquid. The adsorption of particles at the gas-liquid interface requires the transfer of particles from the bulk liquid phase to the interface. Ramsden and Pickering first reported, in the early 20<sup>th</sup> century, that particles with appropriate wettability can stabilize fluid interfaces.<sup>8-9</sup> Since then, it has been well understood that colloidal particles, in the absence of insurmountable kinetic barriers, tend to adsorb irreversibly to fluid interfaces, provided that the particle wettability does not favor one fluid over the other to an extreme degree. Particles with appropriate wettability, usually partially hydrophobic particles with a three-phase contact angle ( $\theta$ ) close to 90° (see Figure 1-3a), will reduce the interfacial tension upon adsorption.<sup>10</sup> Once at the interface, particles are considered irreversibly adsorbed because the minimum energy  $\Delta E$  required to remove a single adsorbed particle of size  $R_p$  from the interface of two fluids with interfacial tension  $\Gamma$  is given approximately by

$$\Delta E = \pi R_n^2 \Gamma (1 - |\cos \theta|)^2 \tag{1-1}$$

For particles within the colloidal domain, typical values of  $\Delta E$  exceed the thermal energy scale, *KT*, by orders of magnitude. In contrast, small surfactant molecules and particles with  $R_p < 1$  nm, can readily adsorb and desorb at the interface. Long-term stability is observed in particle stabilized foams, in comparison their surfactant counterparts, because irreversibly adsorbed particles that lower the interfacial tension and achieve high interfacial coverage limit further coalescence of bubbles



Figure 1-3 Cartoon showing three-phase contact angle of a) a droplet formed on a surface surrounded by another fluid and b) a particle adsorbed at the interface of two fluids.

#### 1.2 Ternary Fluid-Fluid Particle Systems

Ternary mixtures are composed of immiscible fluids, usually water, a waterimmiscible solvent ("oil") or air, and solid particles of different surface characteristics.<sup>11-</sup> <sup>13</sup> Fluid/fluid/particle mixtures have recently become the subject of enormous research because of the various material processing benefits that these mixtures afford. The adsorption of particles at fluid-fluid interfaces allows for the creation of functional materials that have varying structures and well-defined properties. Popular examples of such materials include emulsion gels, colloidosomes, liquid marbles, etc.<sup>14-15</sup> The flexibility and chemistry of fluid/fluid/particle mixtures allows such materials to be adapted for applications in multiple industries such as food, cosmetics, pharmaceutical, filtration, catalysis, etc.<sup>16-18</sup>

The structure and morphology obtained in ternary systems are very much dependent on the particle wettability and fluid/fluid/particle ratios.<sup>19</sup> Recently, Velankar categorized the obtainable morphologies of fluid/fluid/particle mixtures in a state diagram as a function of mixture composition and particle wettability.<sup>20</sup> Figure 1-4 shows the structures that can be obtained when two fluids (A, B) are mixed with particles that neutrally wet both fluids, and particles that are partially wetted and fully wetted by fluid B.



Figure 1-4 Possible morphologies that can be obtained in ternary fluid/fluid/particle mixtures. Capillary suspension (a and g) morphologies are obtainable at different particle wettability and fluid concentrations. Pickering emulsions and bridged emulsion gels (f, h and j) are possible at different fluid concentrations when both fluids partially wet the particles. Bijels require neural wetting particles and similar fluid concentrations. Particles aggregates occur in different structures (b-e) when one of the fluids fully wets the particles; the structure obtained depends on fluid ratios. Republished with permission of Royal Society of Chemistry from ref 20 Copyright 2015.<sup>20</sup>

Capillary suspension (a and g) morphologies are obtainable at different particle wettability and fluid concentrations. Pickering emulsions and bridged emulsion gels (f, h, and j) are possible at different fluid concentrations when both fluids partially wet the particles. Bijels require neural wetting particles and similar fluid concentrations. Particles aggregates occur in different structures (b-e) when one of the fluids fully wets the particles; the structure obtained depends on fluid ratios.<sup>20</sup>

It has been observed for some time now, that particles that neutrally wet both fluids ( $\theta$  close to 90°) can arrest spinodal decomposition of partially miscible fluids to form bicontinuous interfacially jammed emulsion gels (bijels).<sup>21-22</sup> Particle stabilized emulsions (Pickering emulsions) can be obtained when one of the fluids partially wets the particles. If the partial wetting fluid is in higher proportions, higher volume fraction, the emulsion is more likely to remain stable. More recently, work has been devoted to understanding ternary systems in which one fluid preferentially wets the particles, which commonly occurs *e.g.* in capillary suspensions.<sup>23</sup>

In 2011, Koos and Willenbacher observed that the addition of a small amount an immiscible secondary liquid to a particle suspension, with mixing, leads to the formation of a space spanning network of particles bridged by the secondary liquid.<sup>24</sup> The capillary suspension formed by the immiscible secondary liquid, is a highly elastic gel with strong capillary forces that hold the particles together. The differences between the modulus and yield stress in capillary suspensions and the neat suspension (without the secondary liquid) extend over multiple orders of magnitude. The nature of the bridging between the particles towards the secondary and primary liquids.<sup>24</sup> As seen in Figure 1-4, when the secondary liquid preferentially wets the particles, pendular bridges are formed between particles in a network structure referred to as the pendular/funicular state (Figure 1-4a). When the continuous fluid medium wets the particles preferentially, the secondary liquid forms polydisperse bridges each of which typically connect several particles and together stabilize a network of particle aggregates in the capillary state (see Figure 1-4g).<sup>25</sup>

#### 1.3 Capillary Foams

Not long after capillary interactions in suspensions were discovered, it was reported that frothing an aqueous particle suspension with a small amount of immiscible fluid (oil) produced a new type of aqueous foams known as capillary foams (CFs).<sup>26</sup> This new type of foam consists of oil coated bubbles that are surrounded by a bridged particle network. Zhang et. al, observed that the synergistic action of oil and particles facilitates the spreading of oil coats around gas bubbles and that the covering of the oil-water interface stabilizes these bubbles against ripening and coalescence.<sup>26-27</sup> The presence of oil-bridged particles in the bulk, as seen in Figure 1-5 below, entraps CF bubbles in a continuous gel like matrix similar to that of capillary suspensions. Capillary foams represent a new quaternary system formed from fluid/fluid/particle mixtures. Capillary foams circumvent the need for particles with appropriate wettability for adsorption at the air-water interface to stabilize foams. It creates a new route to use more hydrophilic particles, better suited for adsorption at the oil-water interface, to stabilize foams.



Figure 1-5 Characteristic structure of capillary foams. Left: (i) schematic of coated bubbles entrapped in a particle gel. (ii) close-up of the particle network spanning the

space between bubbles. (iii) close-up of network particles connected by oil bridges. (iv) schematic of foam bubble coated by a composite film of oil and particles. (v) closeup of oil film and stabilizing particles in a bubble coat. Right: (iv) SEM image of a particle network with (solidified) oil bridges. (vi) SEM image showing inside view of a bubble coat composed of the polymerized oil trimethylolpropane trimethacrylate (TMPTMA) and adsorbed polyethylene (PE) particles. Adapted with permission from ref 26 Copyright 2014 John Wiley and Sons. Adapted with permission from ref 27 Copyright 2017 American Chemical Society.<sup>26-27</sup>

Capillary foams have been observed to offer better long-term stability, up to months after preparation, than its Pickering foam counterparts when readily dispersible hydrophilic particles are used.<sup>26-27</sup> The parameters influencing foamability and stability in capillary foams, such as the oil type and quantity, pH and ionic strength, particle wettability and concentration, have been characterized because these are very important to understanding how these foams can be applied. Capillary foams have also been functionalized by solidifying the oil-phase through UV-radiation and evaporating the aqueous fluid to create solid foams that are light-weight porous materials.<sup>28</sup> As shown in Figure 1-6 below, the potential applications of capillary foams include, but are not limited to, oil spill clean-up, enhanced oil recovery, load-bearing materials, colored foam production, edible foams and skin care or cosmetic products. Foam performance in many of above-mentioned applications is dependent on fundamental understanding and tunability of foam rheology and dynamics, which is lacking in capillary foams. For example, the consistency of cosmetic foam products and mouth feel (e.g., chewy, syrupy, etc.) of edible foams depend on foam elasticity and viscosity and can be determined via rheological measurements.



Figure 1-6 Showing potential applications of capillary foams. Adapted with permission from ref 28 Copyright 2015 American Chemical Society.<sup>28</sup>

#### 1.4 Foam Rheology and Dynamics

Foam rheology considers foam deformation and flow under stress. Understanding foam rheology is quite important for effective foam application in various industrial products and processes. Foams are metastable dispersions of gas in liquid and the underlying rheology of foams results not only from the physical properties of its components but also on the component volume fractions.<sup>29</sup> Although foams are made up

of primarily fluids, and in some cases (Pickering foams, capillary foams) minor quantities of particles, they exhibit both solid-like and liquid-like properties, depending on the applied stress and gas volume fraction in the foam.<sup>30-31</sup> At high gas volume fractions ( $\phi_g > 0.64$ ), conventional surfactant foams are known to deform elastically like a solid under low applied stress because of the tight packing of polyhedral bubbles. When higher stresses are applied to the foam, bubble rearrangement occurs, the foam yields and eventually flows like a viscous liquid. As seen in Figure 1-7 below, high-quality foams have a non-zero yield stress, as opposed to their low-quality counterparts. The observed elastic behavior disappears when the foam quality ( $\phi_g$ ) falls below random close packing fraction, which for spheres corresponds to  $\phi_{rcp} = 0.64$ .<sup>32</sup> At low foam quality ( $\phi_g < \phi_{rcp}$ ), SFs behave like a bubbly liquid as a result of the loose packing of spherical bubbles within the continuous phase.<sup>31</sup>



Figure 1-7 Plot of stress versus foam quality ( $\phi_g$ ) showing exponential increase in the value of the yield stress required to cause irreversible deformation to the foam. Republished with permission of IOP from ref 31 Copyright 2005.<sup>31</sup>

The physical processes that occur within the foam also influence its rheology. As previously stated, foams drain and coarsen due to actions of gravity and capillarity respectively. The actions of drainage and coarsening are coupled because the liquid and gas volume fractions are not independent of each other; as such the rate of gas diffusion and bubble coalescence is related to the rate of fluid loss from the foam. As illustrated by the schematic in Figure 1-8, the continual evolution of the foam over different length and time scales significantly affects the observed foam rheology. In some instances, foam rheology can be exploited to learn how these processes affect the mechanical properties in foams; for example, the effects of coarsening on foam rheology can be seen at low frequency regimes of oscillatory experiments on foams.<sup>33-34</sup>





Instability in foams poses a significant challenge to foam rheology studies because long-time scale measurements may be difficult to obtain as the foam composition and properties evolve. This challenge however can be overcome with long-term stable foam such as Pickering foams. The rheology of Pickering foam shows significant differences from surfactant foam in its frequency behavior.<sup>36-37</sup> Particle stabilization may lead to significant changes in the foam rheology due to more rigid interfaces as opposed to the elastic interfaces observed in surfactant based foams.<sup>38</sup> Given the unique architecture of capillary foams, it is not clear how significantly different or similar its rheology is to traditional aqueous foams and other soft materials. To effectively exploit capillary foams, its rheological properties must be well characterized and understood.

When studying foam rheology, the appropriate geometry must selected to provide relevant data for the desired application because the measurements obtained are geometry dependent.<sup>39-40</sup> The ratio between the characteristic length scales of the foam (bubble size, l) and the confining instrument (L), in which the foam is sheared in, determines the observed foam behavior. When  $l \ll L$ , the foam can be described using a continuum approximation; a good example of this is foam flowing through a pipe.<sup>41</sup> Bulk foam behavior in this regime is typically characterized by yield stress, viscosity and wall slip. As mentioned above, foams typically exhibit a yield stress that is dependent on the quality of the foam; higher quality foam has a higher yield stress and vice versa.<sup>42</sup> However foams flowing in a tube/pipe do not necessarily yield nor are sheared in the traditional sense of the term. Rather foams flow in a plug, as in Figure 1-9, by slipping on a thin film of liquid that acts as a lubricant between the bulk foam and the pipe wall. Regardless of the geometry selected to study foam rheology, wall slip should be minimized, by using roughened instrument surfaces or by applying correction methods that adjust for slip in results, to allow for reasonable results.43-44



Figure 1-9 Schematic showing different regimes present in a foam flowing through a pipe. Republished with permission of Annual Reviews from ref 41, Copyright 1988.<sup>41</sup>

Flowing foams have high apparent viscosities that are dependent on both shear rate and foam quality; they are characteristically shear-thinning.<sup>45</sup> Besides foam flow in a pipe, rotational instruments such as Couette and parallel plate geometries have also been used to study foam rheology, and while the results from these geometries are comparable to those of the capillary geometries, it has been observed that the foam is better sheared in a rotational geometry.<sup>46</sup>

Foam flow in microflows, when  $l \approx L$ , is more complex because the foam can no longer be treated as a homogenous phase. For example, when foams flow through porous media in which the bubble sizes are comparable to the characteristic length of the confining region, the flow behavior is subject to the geometry, permeability, and connectivity of the pores because the foam phase separates into its components.<sup>47</sup> Foam in porous media is therefore a gas dispersion surrounded by interconnected liquid lamellae (films). The pore spaces are filled with gas while the wetting fluid occupies the corners of the pores and exist as thin films coating the pore wall. In the microflow regime, bubbles are usually lost to drainage, diffusive ripening and coalescence. On the other hand, new bubbles and lamellae can be regenerated through various propagation mechanisms such as snap-off,<sup>48-49</sup> lamella division,<sup>50-51</sup> leave behind,<sup>52</sup> and bubble pinch-off.<sup>53</sup> The pressure gradient must be larger than the minimum capillary pressure, set by local saturation of the wetting phase and the interfacial tension, for gas flow to occur. At low pore flow rates, capillary and viscous forces are dominant, and as such the flow behavior is easily characterized by the capillary number, which characterizes the relative magnitude of both forces.<sup>54-55</sup> The flow characteristics, viscosity, relative permeability, and fluid distribution are typically set by the number of lamellae present.<sup>44</sup> The understanding of foam mechanics at the pore scale level is applicable in soil remediation and enhanced oil recovery, where foams are used to displace other fluids.<sup>56</sup>

#### 1.5 Enhanced Oil Recovery

Gas injection enhanced oil recovery (EOR) is a tertiary oil recovery method that involves the use of gasses such as steam, methane, and carbon dioxide to displace trapped crude oil from underground reservoirs. Constituting 39% of the EOR, gas injection is significantly important given that only about 30-50% of the original oil in place is recovered through primary and secondary recovery methods.<sup>44</sup> However, gas injection suffers from low yield because of gravity override and viscous fingering inefficiencies that lead to non-uniformity of the flood front as shown in Figure 1-10. The major cause of these inefficiencies is the mismatch of fluid densities and viscosities between the displacing gas and the trapped crude oil.


Figure 1-10 Cartoon comparing free gas (left) and foam (right) assisted enhanced oil recovery. Gas fingering and density override artifacts are observed when free gas is used as opposed to a uniform displacement from observed when foams are used.<sup>57</sup> Republished from ref 57 and adapted from ref 58 Copyright (2012), with permission from Elsevier.<sup>58</sup>

Foamed gas injection has long been used to mitigate the challenges of gas injection. Since the late 20<sup>th</sup> century, foams have been shown to be better displacing fluids for EOR because of their high apparent viscosity and their ability to reduce gas mobility by trapping the gas within liquid barriers.<sup>58-60</sup> Significant work and progress has been made in trying to understand and improve foam assisted EOR by studying oil displacement in porous media templates. However, surfactant foams are not stable in the presence of oil and are quite intolerant of the harsh temperature and saline reservoir conditions. Particle stabilized foams have been studied and shown to perform better than surfactant foams due to their ability to reduce and delay the entrance and spreading of oil droplets that destabilize foam films.<sup>61</sup> Given the long-term stability of capillary foams through the synergistic actions of oil and particle, it is possible that capillary foams will prove more effective at displacing crude oil from underground reservoirs.

### **1.6 Thesis Motivation and Objectives**

The performance of foams in formulations and industrial applications depends on foam stability and rheology under stress. For example, in enhanced oil recovery, stable and viscous foams are required to displace crude oil from underground reservoirs. The newly discovered capillary foams, being surfactant-free, oil resistant, long lasting, and potentially tunable, provide new opportunities for foam applications in products and processes that are hindered by the above-mentioned limitations of traditional foams. However, the structural uniqueness of capillary foams suggests that capillary foam rheology might differ significantly from traditional foam rheology and that bubble deformation and foam collapse that can occur during foam flow may be mitigated by the interparticle bridging in CFs. The focus of this work is to investigate the rheology and dynamics of capillary foams for use in products and processes with the following objectives in view:

- a) Determine the rheological properties of capillary foams and understand how these properties can be altered.
- b) Understand how capillary foams flow in bulk and in porous media environments.
- c) Determine the feasibility of using capillary foams to displace crude oil from porous media

### 1.7 Thesis Outline

The remainder of this thesis is outlined as follows:

Chapter Two presents a fundamental study on the rheological properties of capillary foams by using multiple experimental tests to examine the viscoelastic nature of capillary foams. Chapter Three thoroughly investigates how the microstructure affects the rheological properties in capillary foams and provides understanding of how to alter the foam structure and rheology by varying constituent elements.

Chapter Four explores the dynamics of capillary foams flowing in cylindrical tubing and elucidates the effects of shear stress and aging on pumped capillary foams.

Chapter Five investigates the behavior of capillary foams in porous media and explores the potential for using capillary foams to displace crude oil from a micromodel

Chapter Six summarizes the findings of the research work conducted in the above chapters, expounds on the current limitations of capillary foams, and presents recommendations for future work on this research topic.

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### CHAPTER 2. RHEOLOGY OF CAPILLARY FOAMS<sup>1</sup>

### 2.1 Introduction

Foams are widely applicable in a variety of products and processes across different industries because of their rheological properties. For instance, foams provide sensory benefits in foods and beverages like whipped cream, chocolate mousse, and beer.<sup>1</sup> Foams also find extensive applications in the cosmetics, pharmaceutical, material processing, and energy industries.<sup>2-7</sup> The rheological properties of surfactant foams (SFs) have previously been studied for various foam applications. As mentioned in section 1.4, SFs with high gas volume fractions (= high "foam quality") behave either as solids or liquids depending on the applied stress.<sup>8</sup> When a small stress is applied to a foam, it deforms elastically like a solid. Oscillatory measurements show that the elastic modulus of SFs depends on the surface tension between the fluids and the mean bubble size.<sup>9-10</sup> These measurements also reveal a linear regime at low strain where both the storage and loss moduli are independent of the applied strain amplitude. At strains beyond the linear regime, the foam transitions from a solid-like to liquid-like response. This yielding behavior is observed when the applied stress is strong enough to separate and rearrange neighboring bubbles.<sup>11-12</sup> In this case, the foam flows like a liquid as bubbles slide past each other.<sup>9, 13</sup> When the applied stress is removed, flow stops and bubbles relax to a new configuration.<sup>14</sup> Many of these rheological properties of SFs are similar to those observed in other soft dispersion systems, including concentrated emulsions, pastes, and dispersions of microgel beads.<sup>8, 15-17</sup>

<sup>&</sup>lt;sup>1</sup> This chapter has been adapted from the publication Okesanjo O. et al, Rheology of capillary foams. *Soft Matter* **2020**, *16* (29), 6725-6732 and is reproduced by permission of the Royal Society of Chemistry.

With their oil-coated bubbles embedded in a particle network,<sup>18</sup> CFs are structurally distinct from the traditional aqueous foams described above, but somewhat similar to other soft materials: emulsions, capillary suspensions and colloidal gel foams.<sup>19-21</sup> The crucial differences between CFs and colloidal gel foams are that, in CFs, oil-mediated capillary forces provide the attractive particle-particle interactions and that the particles do not stabilize a gas-water interface, but rather the oil-water interface of oil-coated bubbles. Given the similarities and differences that CFs share with other dispersion and colloidal systems, one might speculate that CF rheology is governed by generic responses observed in these other soft dispersion systems.<sup>22</sup> However, the rheology of CFs has never been studied. The purpose of this chapter is thus to take a first look at CF rheology and how it deviates from the rheology of traditional surfactant and Pickering foams, as well as capillary suspensions.

In this chapter, we present the first set of rheological data on capillary foams. We conduct oscillatory and steady shear experiments on a rheometer using parallel plate and Couette geometries. We then outline and discuss CF properties and compare our observations to the rheological properties reported for traditional aqueous foams and other soft materials.

### 2.2 Experimental Section

### 2.2.1 Capillary Foam Preparation

Polyvinyl Chloride particles (PVC, Vinnolit SA1062/7, particle density: 1.41 g/cm<sup>3</sup>, average particle size 14.5  $\mu$ m) were obtained from Vinnolit, Germany.<sup>23</sup> Trimethylolpropane trimethacrylate (TMPTMA) was obtained from Sigma-Aldrich.

Deionized (DI) water with resistivity 18.2 M $\Omega$  ·cm was used as the aqueous phase. Foams were prepared using a rotor-stator homogenizer (IKA Ultra-Turrax T10, rotor diameter of 6.1 mm, stator diameter 8 mm).

Capillary foams were prepared by frothing a mixture of PVC particles (10 wt. %), TMPTMA (2 wt. %) and DI water (88 wt. %). Two grams of PVC particles were first suspended in DI water and sonicated for 1 h (VWR, B2500A-MT). Once sonication was completed, TMPTMA was added to the suspension and the mixture was homogenized at 30,000 rpm for 3 min.

### 2.2.2 Rheology Measurements

An Anton Paar MCR 501 parallel plate (PP) rheometer equipped with a temperature controller and evaporation blocker was used to perform rheological measurements on capillary foams. Shear localization and wall-slip of the foam within the confines of the measuring instrument are known to lead to inaccuracies in rheological measurements.<sup>2</sup> As such, the top plate (diameter of 40 mm) was lined with sandpaper ( $\cong$ 130  $\mu$ m grain size, Porter Cable) to minimize slip in the measurements. A Couette geometry (bob length and diameter: 40 mm, 21 mm; cup diameter: 23 mm) was also used to obtain high shear rate data in controlled shear rate experiments. No sandpaper was used in the Couette bob or cup.



Figure 2-1 Parallel plate setup for making rheology measurements on capillary foams

The prepared capillary foams were transferred carefully to the bottom plate (or Couette cup) of the rheometer. The gap height between the top and bottom plates was set to 4 mm, so that a substantial amount of foam could fit between the plates and account for the one-tenth rule of thumb for dispersed phases.<sup>2</sup> All measurements, unless stated otherwise, were obtained at this gap height. The temperature was maintained at 25°C and the evaporation blocker was used to prevent drying of the foams. Once loaded, the CFs were allowed to rest for 20 min before the start of any steady or oscillatory shear experiments. Frequency sweep oscillatory measurements within the linear viscoelastic regime were obtained before and after each experiment to assess the state of the foam. Strain rates ( $\dot{\gamma}$ ) in both the PP and couette geometries vary across the plate or cup radius; thus, values of  $\dot{\gamma}$  reported are apparent. The data presented here was replicated using fresh samples of CFs to ensure reproducibility.

### 2.3 Results and Discussion

### 2.3.1 Controlled Stress and Strain Rate Experiments

Capillary Foams were subjected to controlled shear stress (CSS) and controlled strain rate (CSR) tests; both tests are steady rotational tests in which the foam is either held at a specific stress or strain rate respectively. Figure 2-2 shows the stress-strain rate curve (flow curve) from the CSS and CSR experiments; the differences between the curves are due to slight changes in gas volume fraction of the foam in the different experiments. The plot shows an initial increase in the stress with strain rate, followed by a stress plateau over a wide range of strain rates. At strain rates higher than those reported for the parallel-plate geometry, we observed that the CF was ejected from the gap between the rheometer plates. However, CSR experiments conducted in the Couette geometry, to obtain higher strain rate data on the CFs, show a later increase in stress; see orange diamond data at the highest strain rates.



Figure 2-2 Plot of stress versus strain rate of the CF; blue inverted triangles and violet cross (repeat) are obtained from controlled shear stress (CSS) experiments on a

# parallel plate (PP) setup; green triangles (PP), black circles (repeat on PP) and orange diamonds (Couette) are obtained from controlled strain rate (CSR) experiments; open red squares are obtained from creep experiments on PP.

From the flow curve in Figure 2-2, we observe two different regimes where the stress ( $\sigma$ ) increases with strain rate at low and high strain rates, and a third regime where the stress is not dependent on strain rate. Generally, for viscous liquids  $\sigma \propto \dot{\gamma}$ , while for elastic solids  $\sigma \propto \gamma$ , and  $\sigma \neq f(\dot{\gamma})$ .<sup>24</sup> The existence of these three regimes in the flow curve of CFs poses an important rheological question about the exact behavior of CFs: are CFs solid or are they a very viscous liquid? The key to this question resides in how to interpret the decrease in  $\sigma$  with decreasing  $\dot{\gamma}$  to the left of the stress-plateau as this can correspond to the aging of a solid foam, or to a final long-time relaxation of a very viscous foam. The flow curve itself is insufficient to answer this question. We thus perform oscillatory tests to characterize the elastic and viscous response of the foams and better understand their rheological properties.

### 2.3.2 Strain Amplitude Sweeps

CFs were subjected to increasing strain amplitudes ( $\gamma$ ) at a constant frequency ( $\omega$ ) of 1 rad/s. Figure 2-3 shows the storage (G') and loss (G'') moduli of CFs and highlights the linear and non-linear regimes of CFs within the range of the applied strain amplitudes (10<sup>-4</sup> to 10<sup>1</sup>). The linear regime is the plateau region at low  $\gamma$ . For  $\gamma < 0.5$ , the CF behaves like an elastic solid, having an elastic response (G') greater than the viscous response (G''). At a strain amplitude of 0.5, we observe a crossover between G' and G'' indicating a yielding transition from a solid-like to a liquid-like response. Above strains of 0.5, G'' is greater than G', indicating that the foam is fluidized and that the bubbles and capillary network are significantly strained and forced to rearrange. We also observed that the normal force on the top plate of the instrument gradually decreases during the strain sweep. The normal force does not recover when the strain sweep is repeated, reflecting a large strain induced structural rearrangement. The decreasing normal force is most likely due to bubble collapse, or to ejection of CFs from between the plates during fluidization.



Figure 2-3 Plot of G' (filled square) and G" (open square) versus the strain amplitudes tested at  $\omega = 1$  rad/s.

The origin of the elastic properties observed in CFs, can be compared to those of SFs. CFs at 10 wt. % particle and 2 wt. % oil concentrations have an average foam quality of 32% (see Figure A-2 in the appendix), which corresponds to half the gas volume fraction where solid-like foam behavior is usually first observed in SFs. At the present foam quality, typical SFs are considered bubbly liquids containing loosely packed spherical bubbles. Rheology experiments show that low-quality SFs have no elasticity.<sup>25</sup> Although CFs may be classified as low-quality foams, their rheology shows a remarkably high elastic response comparable to that of high-quality SFs. Such strong elasticity is also observed in low

quality colloidal gel foams, whose rheology one might expect to be similar to that of CFs.<sup>19</sup> Given that the gelled particle network occupies as high as 70 vol. % of the CF matrix, the elasticity of CFs is likely a result of the strong particle network that both encloses the bubbles and percolates the space between bubbles. For SFs, the elastic shear modulus is  $G \sim \Gamma_{aw}/R$ , with  $\Gamma_{aw}$  the surface tension between the fluids and *R* the mean bubble radius.<sup>26</sup> In contrast, for CFs, *G* is likely to depend on the concentration of particles in the foam, the strength of the capillary bridges in the particle network and the surface energy of the dual fluid interfaces (air-oil and particle laden oil-water) of the bubbles present in the foam. The concentration of the particles and the strength of the capillary bridges have previously been shown to influence the strength of capillary suspensions, the particle network component of CFs.<sup>27</sup>

The nonlinear response in the strain sweep also highlights another key difference between CFs and SFs. As the applied strain increases, CFs and SFs respond differently in the transition region. In SFs, G'' increases within the transition region as a result of Marangoni flows between stretched and compressed bubbles.<sup>9, 28</sup> An increase in G'' is not observed in CFs, suggesting that the rigid particle network structure, stabilized by the capillary bridges between the particles, prevents bubble deformation in the transition region. In fact, this behavior is observed in Pickering foam systems with significant steric barriers that prevent immediate destruction of bubbles.<sup>28-29</sup> In these systems, it was found that while bubble deformation occurs as both moduli decrease, bubble motion does not occur until the crossover between G' and G'' is reached.

Although the results of the strain sweep experiment on CFs show that G' > G'' in the linear "equilibrium" regime at low strain amplitudes and  $\omega = 1$  rad/s, many viscoelastic materials show a frequency dependence. For this reason, the rheological response of CFs was probed with respect to time and frequency.

### 2.3.3 Time and Frequency Sweeps

The equilibrium structure and time-dependent response of CFs were probed in both time and frequency sweep experiments by applying an oscillatory strain within the linear regime ( $\gamma = 0.001$ ). The storage and loss moduli of the CF were monitored at 10 rad/s for 48 h in the time sweep experiments. Figure 2-4a shows the long-time sweep experiment on the CF. The time sweep experiment shows that both elastic and viscous moduli of the CFs are stable over the course of two days; G' and G'' are essentially constant up to  $2 \times 10^4$  s and only slightly increase afterwards. In the architecture of CFs, bubbles are not only connected in a space-spanning particle network but are also enclosed by two fluid-fluid interfaces (oil-air and oil-water). The effects of bubble and particle network connectivity and dual fluid interfaces produce long term foam stability that allows for persistence of the foam rheological response over time. This long-term stability is remarkable given that the continuous evolution of foam structure typically limits the experimentation time in foam rheology measurements. This type of rheological stability is not common among SFs because they tend to be subject to more rapid bubble coalescence and collapse. It is worth mentioning that Pickering foams and colloidal gel foams are perhaps the only other type of aqueous foams that may be capable of similar stability because of the presence of a particle network or particle packing that kinetically stabilizes the fluid interface.<sup>19, 30</sup>



Figure 2-4 a) Plot of G' (filled squares) and G" (open squares) for time sweep measurement at  $\omega = 10$  rad/s on the CFs. b) Plot of G' (filled circles) and G" (open circles) for frequency sweep at  $\gamma = 0.001$  on CFs. c) Plot of G' (filled symbols) and G" (open symbols) for frequency sweep on colloidal gels and gel foams (adapted with permission from Ref. 19 Copyright 2017 American Chemical Society).<sup>19</sup> d) Plot of G' (open symbols), G" (filled symbols) for frequency sweep on surfactant foams; symbols denote the imposed strain amplitude (adapted with permission from Ref. 31 Copyright 2003 American Physical Society).<sup>6, 31</sup>

The frequency sweep plot in Figure 2-4b shows both viscous and elastic response of the CFs over a wide range of frequencies. A stronger elastic response is observed at all frequencies probed; however, G' is observed to increase monotonically. When the foam is probed from high to low frequencies, G" decreases, exhibits a minimum and subsequently increases again. We believe that the increase in G" and decrease in G' toward low frequencies is a result of bubble coalescence and particle network rearrangements within the CF matrix. The frequency sweep data for both CFs and high quality SFs highlights the kinetic changes that occurs in both foam types, showing that aging can lead to structural rearrangements that cause G' G" over long periods of time.<sup>31</sup> Although the elasticity of CFs arises from the particle network in their gel matrix, their frequency dependent behavior is qualitatively similar to that of particle-free SFs, see Figure 2-4b & d. Although  $G'' \sim \omega^{1/3}$  in CFs at high frequencies, in contrast to the  $\omega^{1/2}$  dependence reported for SFs,<sup>22</sup> the moduli obtained from the frequency sweep experiments suggest that CFs are more similar to SFs than to colloidal gel (Pickering) foams in their time dependent behavior.<sup>19</sup> Note, however the differences in the values of the moduli: both the G' and G" values of CFs are significantly larger than those of typical SFs.

The qualitative similarity of capillary foams and surfactant foams in the frequency sweeps suggests that in both systems it is the bubble network that determines the overall flow behavior, even though the mechanical coupling between bubble deformations occurs through the particle network in CFs and through direct contact in SFs. The weaker frequency dependence of G'' (lower exponent) at high frequencies in CFs indicates a less pronounced dissipation in this regime, which could result from the presence of rigid structures. This is consistent with the observed lower frequency dependence ( $G'' \sim \omega^{\nu}$  with  $\nu < 1/2$ ) in SFs with high interfacial rigidity due to the presence of co-surfactants with low water solubility.<sup>32</sup> In CFs bubble rigidity stems from the bubbles' composite coat of oil and particles and its coupling to a stiff network of oil-bridged particles that further contributes to diminishing dissipation and thereby shifting the short time relaxation ("beta relaxation") to higher frequencies (shorter time scales).

Above all the oscillatory tests show that the unique structure of CFs leads to distinct foam rheology that sets these foams apart both from previously studied colloidal gel foams, and from traditional surfactant stabilized foams. The frequency sweep also helps determine the characteristic relaxation time ( $\tau_c$ ) of the CFs corresponding to the crossover of G' and G" at low  $\omega$ .<sup>24</sup> We determine  $\tau_c$  from the crossover frequency  $\omega_c$ :

$$\tau_c = \frac{2\pi}{\omega_c} \tag{2-1}$$

By extrapolating the data in Figure 2-4b to lower frequencies, G' and G" are expected to intersect at  $10^{-4} < \omega_c < 5 \times 10^{-4}$  rad/s. The relatively long characteristic time (~10<sup>4</sup> s) observed in CFs is similar to the characteristic time of SFs.<sup>31</sup> However, while the slow linear viscoelastic response in SFs results from coarsening of the foam and Marangoni flows in the foam's liquid films, the timescale of the slow viscoelastic response of CFs is dictated by particle network rearrangement over time. CF rheology suggests that G' < G'' at low frequencies because aging unjams the CFs over time. The onset of this long-time viscous dominance occurs on timescale on the order of  $\tau_c$ .

### 2.3.4 Stress Relaxation

To further study the rheological behavior of the CFs, stress relaxation experiments were performed by applying a constant strain to the foam while monitoring the time dependence of the stress.<sup>33</sup> Figure 2-5 shows the result of stress relaxation experiments

performed on CFs. The unperturbed response of the CF corresponds to the blue curve, where a strain of zero ( $\gamma \ll 10^{-6}$ ), within the limits of the rheometer, is applied.



Figure 2-5 Plot of stress over time on CFs during stress relaxation experiments. Symbols correspond to applied strains below 10-6 (blue squares), applied strain in the linear regime at  $\gamma = 0.005$  (red circles), applied strain outside the linear regime at  $\gamma = 0.01$  (black triangles). The black line in the inset shows an exponential fit.

For a strain of  $\gamma = 0.005$  within the linear regime (see Figure 2-3), we observe in Figure 2-5 that the stress on the foam significantly relaxes after ~6 h (22,000 s); the relaxation time, obtained by fitting this stress decay to an exponential function, is  $4.6 \times 10^4$  s and thus comparable to the  $\tau_c$  obtained from the frequency sweep experiment. The relaxation behavior observed in CFs is typical of viscoelastic materials and confirms that  $\tau_c$  predicted by the frequency sweep is indeed a result of relaxation processes. Note that for a strain of  $\gamma = 0.01$  which is outside the linear regime (see Figure 2-3), the stress on the foam never recovers during the experimental time, indicating that plastic deformation has occurred.

### 2.3.5 Creep Experiments

Creep experiments were performed to study in detail the long-term behavior of the CFs under stress. In these experiments, we applied a constant stress and measured the time dependence of the strain. Figure 2-6 shows the strain response at applied stresses ( $\sigma$ ) ranging from 0.5 Pa to 50 Pa. All plots show a general trend of three strain regimes that include an initial fast strain increase, a transition zone and a linearly increasing strain.



Figure 2-6 Plot of strain versus time in creep experiments; a) with applied stresses at 50 Pa (green triangles), 30 Pa (red circles), and 10 Pa (black squares). b) Plots of lower stresses at 10 Pa (black squares), 5 Pa (blue circles), 1 Pa (pink stars), 0.5 Pa (orange inverted triangles) and 0 Pa (violet triangles). Black dashed lines show linear fits used to obtain  $\dot{\gamma}$ .

The fast initial strain increase corresponds to the short-time elastic response of the material to the applied  $\sigma$  while the linear increase in strain is indicative of a long-time viscous behavior. From the linear fits in this region, we obtain  $\dot{\gamma}$ . By further using the value of the applied stress, the viscosity is obtained from Equation 2-2

$$\eta = \frac{\sigma}{\dot{\gamma}} \tag{2-2}$$

The result of the creep experiments indicates that CFs exhibit viscous flow over long time periods even for minute applied stresses. When an infinitesimal stress ( $\sigma = 0 Pa$ ) is applied to the CFs, the instrument measures a strain increase over the experimental time, see violet triangles in Figure 2-6b. This strain increase, which is on the order of  $10^{-4}$ , is within the detection limits of the instrument, which is  $\gamma \ge 10^{-6}$ , and is taken to be the strain increase of the unperturbed CF. We believe that this minute strain increase is caused by coarsening and particle network restructuring that results from the non-equilibrium nature of foams as seen in the frequency sweep experiments. When  $\sigma = 0.5$  Pa or 1 Pa, the strain increase measured is similar to that obtained when  $\sigma = 0$  Pa. However, for  $\sigma > 5$  Pa, the strain increases by at least an order of magnitude. From Figure 2-7 however, we observe a continuous decrease in  $\dot{\gamma}$  over time, showing that the strain increase induced by the applied stresses results in a non-steady-state flow of the CF. The higher stresses applied (10, 30, 50 Pa) apparently lead to an increased initial rate of structural rearrangements in the foam, but eventually the induced strain rates still decay to the level observed even in the absence of any significant externally applied stress.



Figure 2-7 Evolution of strain rate in capillary foams during creep experiments; magnification of strain rate versus time at longer time (inset). Applied stresses at 50 Pa (green dashes), 30 Pa (red dash dots), and 10 Pa (black line), 0.5 Pa (orange line) and 0 Pa (violet line).

To further elaborate on this, the viscosity (10<sup>7</sup> Pa·s) obtained from the creep experiments and the plateau modulus ( $G_0 = 10^3$  Pa) of G' in the frequency sweep (see Figure 2-4b) are divided to obtain a time scale,

$$\tau = \frac{\eta_{creep}}{G_0} \tag{2-3}$$

which is on the order of  $\tau_c$ , suggesting that the viscous behavior observed in the creep experiments (Figure 2-6) is related to aging events resulting from rearrangements in the foam.

The combined results of the oscillatory, stress relaxation and creep experiments help understand the flow curve of CFs (see Figure 2-2). From the oscillatory and stress relaxation experiments, we find that the CF is a solid undergoing aging on a timescale of  $\tau_c = 10^4$  s. From the creep experiments, we observe that stresses  $\leq 50$  Pa cause small deformation rates ( $\dot{\gamma} \ll 1/\tau_c$ ), indicative of particle network rearrangements. These results confirm that the CF flow curve is representative of a solid undergoing aging that yields at sufficiently large stresses.

The CF flow curve is also quite similar to the flow curves of Gillette shaving foams, mayonnaise emulsions and polystyrene suspensions obtained by Da Cruz, et al.<sup>15</sup> The authors in that study also attribute the initial stress increase regime to structural rearrangements within the foam. This explanation is consistent with the results of our creep experiments on CFs, which show that for a given range of applied stresses, decreasing strain rates are observed as the CF relaxes to new configurations. Further work done by Coussot et al. also shows that the plateau in the stress results from the acceleration and deceleration of  $\dot{\gamma}$  at certain stresses.<sup>34</sup> They observed, going from low to high stresses, that below a critical stress value ( $\sigma_{c1}$ ),  $\dot{\gamma}$  continuously decreases with time and that beyond a second critical stress value ( $\sigma_{c2}$ ),  $\dot{\gamma}$  accelerates to a constant value. At intermediate stresses (between both critical stress values),  $\dot{\gamma}$  first increases and then rapidly falls off.<sup>35</sup> While we certainly observed that  $\dot{\gamma}$  continuously decreases below 70 Pa <  $\sigma_{c1}$  <100 Pa, we could not reach values above the second critical stress ( $\sigma_{c2}$ ) before the CFs are ejected from between the gap of the rheometer plates. Data on the CFs could not be gathered beyond a stress of 128 Pa using the parallel plate geometry.

The point at which the stress plateau occurs is said to closely correspond to the value of the yield stress of the material when an increasing stress protocol is used.<sup>34</sup> Flow curves of yield stress materials show that the stress tends to a finite value as the strain rate approaches zero. For example, the reported flow curve of Carbopol microgel, shows a yield

stress on the order of tens of Pascal at a strain rate of  $10^{-3}$  s<sup>-1</sup>.<sup>36-37</sup> From the results of the CSS and CSR experiments here, the estimated value of the yield stress of the CFs is about 100 Pa. The yield stress value obtained for CFs is very similar to that of CGFs, which have  $\sigma_y \sim 110$  Pa,<sup>19</sup> showing again that CFs are highly elastic materials.

While there are disputes concerning the existence of yield stress in soft materials,<sup>38-</sup> <sup>40</sup> the notion of a yield stress and the transition from solid-like to fluid-like behavior in foams have been justified by the observations of Lissajous curves and strain sweeps in oscillatory experiments, start-up shear experiments and flow curves of CSS.<sup>13, 41-42</sup> Although we observe a similar trend in the strain sweeps of CFs, where the loss and storage moduli cross over in the strain sweep plot, sample ejection in parallel plate and slip limitations in Couette geometry prevented us from obtaining the full flow curve of the CFs from CSS experiments. Slip is an experimental artifact that can lead to errors in yield stress determination.<sup>43</sup> Although most of the data presented in this work were obtained using roughened plates, it is possible that the data is influenced by slip. Marze, et al. for instance, observed slip contributions to their foam rheology data despite using rough shearing surfaces; they commented that slip existence is dependent on both the applied shear rate and plate roughness.<sup>44</sup> When smooth shearing surfaces are used, as is the case in the Couette experiments here, three different slip regimes are observed. Meeker et al. observed that for  $\sigma \ll \sigma_{\nu}$ , motion is due to wall slip, for  $\sigma \approx \sigma_{\nu}$ , motion is due to both slip and yielding contributions, and for  $\sigma \gg \sigma_y$  slip is negligible.<sup>17, 45</sup> The decrease in stress observed at  $0.1 < \dot{\gamma} < 100 \text{ s}^{-1}$  during the CSR experiment in the Couette geometry (orange diamond plot in Figure 2-2) could then reflect the stress-induced structural rearrangement prior to yielding and the possible influence of slip. At lower  $\dot{\gamma}$ , the accurate

determination of the yield stress of CFs, requires the careful study of the exact nature and extent of slip in the experiments; this could be done using microscopic techniques.<sup>43</sup> Alternately, a vane geometry, which has been shown to effectively suppress slip effects in structured fluids, can also be used to increase the accuracy of the yield stress determination.<sup>46</sup> The experiments conducted here are thus to be taken as the first estimate of this quantify for CFs.

The yield stress in this CF is lower than the yield stress (of ~ 400 Pa) inferred from measurements on the capillary suspensions that form the continuous phase of the CF, and lower also than values reported previously for other capillary suspensions  $(\sigma_{y,cs} \sim 300 - 10,000 \text{ Pa})$ ,<sup>20, 47-48</sup> but falls within the range of the yield stresses reported for some SFs and Pickering foams ( $\sigma_{y,foam} \sim 20 - 200 \text{ Pa}$ ).<sup>15, 28, 41</sup> Although the yield stress in suspensions and foams is typically governed by the volume fraction of a single dispersed phase, the notion of yielding as the result of dispersed moieties unjamming still likely applies in those materials and CFs alike.<sup>6, 22, 27, 30</sup>



Figure 2-8 Viscosity versus strain rate plot corresponding to the flow curve in Fig. 2. Blue inverted triangles and violet cross (repeat) are obtained from controlled shear stress (CSS) experiments on a parallel plate (PP) setup; green triangles (PP), black circle (repeat on PP) and orange diamonds (Couette) are obtained from controlled strain rate (CSR) experiments; open red squares are obtained from creep experiment on PP.

Lastly, in Figure 2-8, we plot the viscosity of the CFs as a function of the strain rate. The plot shows that CFs shear thin after they yield. At low strain rates, the CFs behave 'extremely viscous', having viscosities  $10^{10}$  times the viscosity of water. As seen from the creep experiments, the viscosity at  $\dot{\gamma} \leq 10^{-5} \text{s}^{-1}$  result from the restructuring (aging) of CFs and are non-steady state viscosities. At higher  $\dot{\gamma}$ , the viscosity decreases with increasing strain rate with a slope of -1, corresponding to the plateau region of the flow curve. CSR experiments show that the shear thinning behavior of CFs at high strain rates is similar to that of surfactant foams described in the literature.<sup>41, 49-50</sup> Even at the highest strain rates observed, the viscosity of the CFs studied here remains significantly higher than the viscosity of water.

The rheological data presented in this work characterizes CFs as an aging solid because of their out-of-equilibrium nature. The behavior observed in CFs is similar to that of crystalline solids like ice that are known to flow at long time scales.<sup>51</sup> While the apparent fluid nature in crystalline solids is defect mediated, the non-equilibrium nature in foams results in the observed aging. Aging has also been observed in similar out-of-equilibrium soft materials like emulsions and microgels.<sup>52-53</sup> The aging dynamics of CFs, though beyond the scope of this work, resembles the glassy dynamics of disordered hard materials and might be understood using models of soft glassy rheology.<sup>54</sup>

### 2.4 Conclusion

The rheological properties of capillary foams have been investigated by carrying out oscillatory and steady shear rotational measurements. Reproducible measurements of this kind are greatly facilitated by the excellent long-term stability of capillary foams. The results show that capillary foams (CFs), despite their low gas volume fraction (low "foam quality"), are rheologically quite similar to high quality surfactant foams. Oscillatory measurements on the CFs at a frequency of 1 rad/s reveal the dominance of elastic behavior over viscous behavior, which is not known from low quality surfactant foams but has been observed in low quality colloidal gel (Pickering) foams, albeit with a very different frequency dependence of the viscoelastic moduli than reported here for CFs. Time sweep experiments lasting 48 h show consistent elastic and viscous responses of CFs with slight increases to both moduli after 10<sup>4</sup> s. The strong elastic properties and long-term stability observed in CFs are results of the oil-stabilized particle network and particle-stabilized oil coat surrounding the bubbles. Frequency sweeps and stress relaxation measurements indicate that the characteristic relaxation time of CFs is on the order of 10<sup>4</sup> s and that CFs exhibit plastic deformation when subjected to high strains. Creep experiments on CFs show short time elastic response and foam restructuring over long time periods. Results from

creep, controlled stress and strain rate experiments are all consistent with a yield stress in CFs on the order of 100 Pa and a long-time aging behavior. Controlled strain rate measurements also show that CFs possess high viscosities and are shear thinning after yielding in the non-linear regime. The high viscosity observed here, in conjunction with the known CF stability against contact with an oil phase, suggests that CFs could be useful as displacing fluids in enhanced oil recovery. We believe that the unique structure and composition of capillary foams and their resulting rheological properties offer further opportunities for foam related innovations ranging from low fat foods to novel foam formulations for health care, cosmetics, and household products. In the coming chapters, we will explore important factors and parameters that influence capillary foam rheology.

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## CHAPTER 3. STRUCTURE-PROPERTY RELATIONSHIP IN CAPILLARY FOAMS<sup>2</sup>

### 3.1 Introduction

Controlling the properties of ternary colloidal multiphase systems plays a big role in material design and processing in the ceramics, food, pharmaceutical and cosmetics industries. In many of these ternary fluid/fluid/particle systems, capillary interactions, constituent volume fractions and particle wettability determine the stability and properties of the observed structures.<sup>1-2</sup> Pickering emulsions, liquid marbles, and bijels are examples of different ternary states obtainable when particles interact at fluid-fluid interfaces.<sup>3-5</sup> CFs, having three, not two, immiscible fluids are distinct and are not represented in the prism of ternary mixtures shown in section 1.2.<sup>6</sup> Indeed, the constituent elements of CFs, including bubbles, oil, water, and particles, all come together to establish the unique properties that have been observed in CFs.

Given the uniqueness of CFs, its structure-property relationship cannot be obtained or extrapolated from the results of the previous work on ternary systems. While the effects of the type and concentration of oil and particles on the foamability and stability of CFs have been qualitatively characterized from a macroscopic perspective,<sup>7</sup> the effects of the CF composition and the particle wettability on the structure and mechanical properties of CFs is unknown. To effectively engineer CFs for use in various products and processes, it is important to understand how CF morphology and rheology vary with its constituent ratios

<sup>&</sup>lt;sup>2</sup> This chapter has been adapted with permission from Okesanjo, O., et al, Structure-Property Relationship in Capillary Foams. *Langmuir* **2021**, *37* (35), 10510-10520. Copyright 2021 American Chemical Society
and wettability as this knowledge provides fundamental understanding of multiphase quaternary systems and how they differ from ternary systems.

In this chapter, we study the influence of constituent variations on the microstructure and rheology of CFs. We vary the stoichiometry of the condensed matter components, but do not control the amount of gas incorporated, because unlike the amount of secondary liquid in a capillary suspension, the gas volume fraction in CFs cannot be varied easily and directly but is determined, for a given frothing procedure, by the stoichiometry of the foam's solid and liquid components. Microscopy, rheology and foamability experiments are carried out to determine how the particle wettability, and the constituent ratios affect the rheology and microstructure in capillary foams. The observed CF microstructures and obtained rheological measurements as well as their effects on CF properties such as foamability and foam stability are outlined and discussed in detail. Lastly, we compare our results to what has been reported on capillary suspensions and discuss the implications of these results in relation to the tuning of CF properties for potential applications.

# 3.2 Experimental Section

#### 3.2.1 Materials

Amorphous fumed silica particles partially modified with dichlorodimethylsilane were provided by Wacker-Chemie AG (Germany); they retained 50% residual silanol groups on the surface according to the vendor. Two more strongly hydrophobized types of fumed silica particles were provided by Evonik (USA): Aerosil R 972, also modified by dichlorodimethylsilane, and Aerosil R 812S, modified by hexamethyldisilazane (HMDS). Trimethylolpropane trimethacrylate (TMPTMA), a photopolymerizable solvent used in several previous studies as the foam's oil component, was obtained from Sigma-Aldrich. De-ionized water was used as the aqueous continuous phase for the CFs. All foams were prepared using a rotor-stator homogenizer (IKA Ultra-Turrax T10, rotor diameter of 6.1 mm, stator diameter 8 mm).

## 3.2.2 Particle Dispersion

Silica particles were initially dispersed in methanol. The particle solution was centrifuged, and the methanol supernatant was removed. The particle sediment was rinsed with DI-water by first re-suspending the particles in DI-water, sonicating the solution to properly disperse the particles and finally centrifuging the solution. The particles were rinsed at least five times to effectively remove the methanol.

## 3.2.3 Particle Characterization

Particle sizes and zeta potentials were determined by dynamic and electrophoretic light scattering using a Malvern Zetasizer Nano ZS90. The hydrodynamic radii and zeta-potentials of the silica particles were obtained in 5 mM sodium chloride (NaCl) solution. The relative wettability of the silica particles by the two liquid foam components was characterized qualitatively by determining their 'preferred emulsion type', *i.e.* the type of emulsion (o/w or w/o) formed when mixing equal volumes of TMPTMA and aqueous (0.1 wt. %) particle dispersion. Table 3-1 lists the particle properties and emulsion types stabilized by the particles used in this work.

Particle Identifier	Particle Name (Supplier)	Size <sup>a</sup> (nm)	Zeta- Potential <sup>a</sup> (mV)	Emulsion Formed	Comments
$\mathbf{P}_1$	HDK H30 (Wacker)	466 ± 27	$-25.3 \pm 1.3$	Oil-in- Water	
P <sub>2</sub>	Aerosil R 972 (Evonik)	594 ± 18	-24.6 ± 0.6	Water-in- Oil	
P <sub>3</sub>	Aerosil R 812S (Evonik)	215 ± 1	-21.6 ± 0.7	Water-in- Oil	Most hydrophobic. The only particles to allow for the production and stabilization of large (Pickering) foam volumes by frothing oil-free dispersions

Table 3-1 Properties of particles used in foaming, microscopy, and rheology experiments.

<sup>a</sup>The uncertainty represent the standard deviation from the average value of 3 independent measurements.

# 3.2.4 Capillary Foam Preparation

Silica particles suspended in DI-water containing 5 mM NaCl salt were prepared in a 20 ml vial. TMPTMA was added to the silica suspension at the appropriate oil-particle ratio. CFs were prepared by mechanically frothing the mixture at 30,000 rpm for 2 minutes, unless otherwise mentioned.

## 3.2.5 Foam Imaging

Confocal images of capillary foams were obtained via laser scanning confocal microscopy experiments on an inverted microscope (Olympus, IX81; 60x, 20x and 4x objectives). An oil soluble fluorescent dye (Nile red) was added to the TMPTMA oil used to prepare the capillary foams. Nile red was excited using a 546 nm laser and emission detected above 650 nm. All microscopy images were processed using ImageJ software.

#### 3.2.6 Rheology Measurements

An Anton Paar MCR 501 rheometer equipped with a temperature controller was used to perform rheological measurements on the capillary foams. A vane geometry tool (diameter = 16 mm, length = 22 mm; cup diameter = 28.9 mm) was used in the rheology experiments to prevent inaccuracies that arise from shear localization and wall-slip in the rheological measurements.<sup>8</sup>

Capillary foams were prepared in the rheometer cup. The temperature was maintained at 25°C. Once prepared, the CFs were allowed to rest for 10 min before the start of the steady and oscillatory shear experiments. Frequency sweep oscillatory measurements at a strain  $\gamma = 0.001$  were obtained before and after each experiment to assess the state of the foam. Results from chapter 2 demonstrates the reproducibility of CF rheology data.<sup>9</sup> Repeat measurements on independently prepared batches suggest a range of uncertainty for the rheology data comparable to the size of the markers (see Figure A-10 in the appendix).

# 3.3 Results and Discussion

#### 3.3.1 Foam Structure

The internal structure of capillary foams was probed by detecting the fluorescence oil phase via confocal microscopy. Figure 3-1(a) is a typical confocal image showing the location of the oil in a thin slice of the capillary foam. Where the image plane cuts through the oil coat surrounding the spheroidal bubbles, bright circles with a dark center can be seen. The oil bridges connecting particles in the gel matrix are too small to be resolved individually, but they contribute to the diffuse 'clouds' of brightness visible in the space outside the bubbles. Spots of intense brightness indicate oil droplets incorporated in the network as well. For a more 3-dimensional impression of the same foam sample, Figure 3-1(b) shows a 'z-stack projection', *i.e.*, the overlay of 163 two-dimensional images of the x-y-plane, such as Figure 3-1(a), taken at different z-positions spanning 81  $\mu m$  in depth. The CF imaged in this figure was prepared with P<sub>1</sub> particles at a particle volume fraction  $\phi_p = 0.92$  % with respect to the total volume of the condensed phases (water + particles + oil) and at an oil-particle volume ratio  $\varrho = 0.2$ .



Figure 3-1 Confocal micrographs showing (a) single image in the XY-plane of capillary foams made with P<sub>1</sub> at a particle volume fraction  $\phi_p = 0.92$  % and an oil-particle ratio  $\varrho = 0.2$ . and (b) z-stack projections of multiple images. Bright regions show the fluorescent oil

As Figure 3-1 illustrates, the network of oil-bridged particles occupies a significant portion of the capillary foam structure. The microstructure observed from the confocal micrographs reveal that bubbles in these CFs are polydisperse, with bubbles sizes ranging from a few microns to hundreds of microns in diameter. By measuring the area fraction of the bubble interior spaces in Figure 3-1b, the gas volume fraction ("foam quality") in this CF is determined to be  $\sim$ 34%.

Apart from oil-coated bubbles and the particle network, oil droplets were also observed within the CFs structure shown in the confocal micrographs in Figure 3-1. The presence of oil droplets in CFs is unexpected, because oil droplets were not observed in previously reported structures and images of CFs.<sup>7, 10-11</sup> The co-existence of oil droplets and bubbles is not unique to CFs, but has been observed in systems sometimes referred to as *foamulsions*,<sup>12-13</sup> in which all of the oil resides in droplets accumulating within the Plateau borders of a denser, particle-free foam. The oil, in water-continuous foamulsions, does not engulf the bubbles, does not bridge solid particles, or stabilize a particle network. Furthermore, the amount of oil droplets as a fraction of the total liquid volume in foamulsions is typically higher than the entire oil per total liquid volume in a capillary foam, and "much higher" than the volume fraction of the newly discovered droplets in some capillary foams. In capillary foam, by contrast, the oil is closely associated with the particles: particles facilitate the spreading of the oil around the bubbles and stabilize the bubble coating layer of oil, and oil bridges are anchored between particles in the gel network. Similarly, it is assumed that adsorbed particles stabilize the droplets of excess oil seen in Figure 3-1; after all, their high affinity for the oil-water interface and preferential wetting by the water phase should also qualify these P1 particles as oil-in-water emulsion stabilizers (see Table 3-1). One should then expect the occurrence and prevalence of bulk oil droplets in the CFs to be a function of the particle wettability and/or the oil-particle ratio. This hypothesis shall be explored next.

## 3.3.1.1 Effect of Oil-Particle Ratio on Capillary Foam Structure

First, we document the changes that occur in the CF microstructure as  $\rho$  is increased in CFs prepared using P<sub>1</sub> particles. Figure 3-2 shows a series of confocal images of the CF structure that were obtained for an oil-particle volume ratio  $\rho$  of 0.2, 0.5, and 1, respectively, at a fixed particle volume fraction  $\phi_p = 0.92$  vol. %. The images in Figure 3-2 show that the number of droplets, visible as intense bright spots in the CFs, increases with  $\rho$ . The number of droplets at the lowest oil-particle ratio ( $\rho = 0.2$ ) is small, with typically only 1-2 droplets in a 212  $\mu$ m x 212  $\mu$ m field of view, whereas much of the visible oil is incorporated in the bubble coats and in the diffuse oil-particle network. At higher  $\rho$ , more of the oil droplets are observed in the CF structure, and at  $\rho = 1$ , the droplets are quite prevalent throughout the CF. Figure 3-2 shows that the excess of oil leads to a CF structure containing many oil droplets as well as a brighter oil-particle network consistent with larger capillary bridges.



Figure 3-2 Confocal micrograph grid of capillary foams at different oil-particle ratios: (a)  $\varrho = 0.2$ , (b)  $\varrho = 0.5$ , (c)  $\varrho = 1$ , all at a constant particle volume fraction  $\phi_p = 0.92$  % of P<sub>1</sub> particles

While the increase in the number of droplets may be trivial, the presence and origin of droplets in the CFs is not. One potential reason why oil droplets were not observed in previous work on CFs<sup>7, 10-11</sup> could be that the oil-particle ratio used in that study was low  $(\rho \sim 0.14)$ . However, when the oil-particle ratio used to make CFs with P<sub>1</sub> here is reduced considerably ( $\rho = 0.05$ ), at least one droplet, per field of view, is observed and micrographs covering a larger area typically show several oil droplets present throughout the foam microstructure. Another plausible reason for the presence of oil droplets in the CF microstructure is that the energy input supplied to the system in the frothing process may have been insufficient to finely distribute the remaining oil across the nascent particle network and bubble surfaces. Previous work on CFs has shown that the gel network has to be formed first before bubbles can be retained in the system.<sup>7</sup> The mixing energy has been observed to have a significant impact on the mechanical properties of the gel network in capillary suspensions and as such could also play a role in influencing the structure observed in CFs.<sup>14</sup> Effective production of CFs used in this work required frothing at the maximum speed of the homogenizing mixer, therefore the effect of mixing energy was not further explored. Apart from the amount of oil and the mixing energy, particle wettability may also determine the location of the oil in the CFs microstructure. Specifically, one might expect that oil droplets will not be accommodated when particles are preferentially wetted by the oil (poor o/w-emulsion stabilizers).

# 3.3.1.2 Effect of Particle Wettability on Capillary Foam Structure

Capillary foams, just like capillary suspensions, can be produced regardless of which liquid preferentially wets the particles (the continuous phase or secondary liquid). The particles' wetting preference does, however, determine the type of inter-particle bridging (pendular bridges *vs* capillary aggregates) that drives gelation and yields, outside the foam bubbles, a capillary suspension in either the pendular or the capillary state.<sup>15-16</sup> Although the particles and oil bridges in the CFs are so small that the exact type of bridging present in the confocal images of both Figure 3-1 and Figure 3-2 cannot be seen directly, the emulsion tests show that the P<sub>1</sub> particles are preferentially wetted by water, because they stabilize a water-continuous emulsion upon mixing equal volumes of the aqueous dispersion and the oil (Table 3-1). For this reason, we believe that the hazy illuminated background seen outside the foam bubbles in Figure 3-1 and Figure 3-2 originates from the oil bridges in the capillary aggregates familiar from capillary suspensions with particles preferentially wetted by the liquid medium. The liquid bridges in the capillary state can be larger and more polydisperse than the pendular bridges, which wet the particles preferentially.<sup>16</sup>

To explore foams in the pendular state, we turn to the more hydrophobic P<sub>2</sub> particles, which are known to be preferentially wetted by the oil (TMPTMA), since they stabilize oil-continuous emulsions of equal liquid volumes (Table 3-1). Figure 3-3 shows confocal images of CFs produced with P<sub>2</sub> particles at a volume fraction  $\phi_p = 0.92\%$ , and different oil-particle volume ratios ( $\varrho = 0.2, 0.5, 1$ ). The first feature distinguishing Figure 3-3a-c from their counterparts in Figure 3-2 is the absence of a diffuse fluorescence signal from much of the space outside the oil coated bubbles. Although the diffuse signal was previously attributed to the oil-particle network in the capillary state, the absence of this signal does not imply the absence of a network in the present case. Instead, we conjecture that the oil-particle network in the pendular state fails to "light up" because the pendular bridges between the particle pairs are too small to yield a significant fluorescence

signal, and thus hinder the observation of the network in confocal imaging. The images in Figure 3-3 also illustrate that, overall, there are significantly fewer oil droplets present in these pendular state foams compared to their capillary state counterparts in Figure 3-2, and again the prevalence of these droplets increases with the oil-particle ratio  $\rho$  (Figure 3-3). While Figure 3-3a could raise doubts whether any droplets are present at  $\rho = 0.2$ , the zoomed-out z-stack projection of Figure 3-3d clearly shows a few oil droplets interspersed between the oil coated bubbles. These droplets are smaller in size and concentration than those seen in the corresponding image of the foam made with the hydrophilic P<sub>1</sub> particles (Figure 3-1b); this shift in size and number of oil droplets in CFs. Note that the CF bubbles obtained with P<sub>2</sub> particles, in many cases, appear closer to each other than the bubbles obtained with P<sub>1</sub> particles, an observation likely linked to the differences between the intervening particle networks as well.



Figure 3-3 Confocal micrographs of capillary foams with a particle volume fraction  $\phi_p = 0.92$  % of P<sub>2</sub> particles at different oil-particle ratios (a)  $\varrho = 0.2$ , (b)  $\varrho = 0.5$ , (c)  $\varrho = 1$ , and (d) a z-stack projection of lower magnification confocal micrographs ( $\varrho = 0.2$ ).

To further illustrate the effects of particle wettability, more zoomed out confocal images of CFs prepared with the three particle types P<sub>1</sub>-P<sub>3</sub> in order of increasing particle hydrophobicity are compared in Figure 3-4a-c. We note that the most hydrophobic particles (P<sub>3</sub>) were found to also stabilize Pickering foams with excellent foamability and foam

stability even in the absence of oil. The capillary foams shown in Figure 3-4, however, were prepared with a (condensed phase) volume fraction  $\phi_p = 0.92$  % of the respective particles and an oil-particle volume ratio  $\varrho = 0.2$ . The confocal images in Figure 3-4 indicate that the prevalence of oil droplets in CFs decreases with increasing particle hydrophobicity and reveals that even in the system with the most hydrophobic particles, oil droplets can still be found, albeit at low concentration.





The oily bubble coats cannot be seen in these images, because of their low magnification. At higher magnification of the confocal images (see Figure A-9), the foam bubbles in all three cases, including the one where particles (P<sub>3</sub>) are hydrophobic enough to stabilize a Pickering foam in the absence of oil, are indeed coated with oil. The images in Figure 3-2, Figure 3-3, and Figure 3-4 show that the capillary foam microstructure changes with particle wettability and confirm that particle wettability influences the number of oil droplets incorporated in the CF at a given oil concentration.

# 3.3.2 Foam Rheology

The interactions within CFs give rise to mechanical foam properties that can be probed using rheometry. In the previous chapter, extensive rheological studies were conducted on a CF containing large micron sized particles in a pendular state network.<sup>9</sup> Here, the rheological similarities and differences that exist between CFs with different particle network states are investigated and the findings are related to rheological differences reported for capillary suspensions in the corresponding states. The influence of the oil and particle content on CF rheology is also examined.

Frequency sweep (FS) and controlled shear stress (CSS) experiments were conducted to probe the rheology of CFs prepared from P<sub>1</sub> particles at different particle volume fractions and oil-particle ratios. The plateau of the storage modulus (referred to as the "plateau modulus"  $G_0$  from here on) and yield stress ( $\sigma_y$ ) of the CFs were obtained from the results of the respective FS and CSS experiments. The storage modulus (G') is a measure of the elasticity and provides an indication of the material rigidity. The plateau modulus in CFs is obtained in frequency sweeps by averaging the flat portions of the storage modulus plot (see Figure A-11b). The yield stress on the other hand measures the resistance to flow in a material. The concept of yield stress in complex fluids is still a debated topic,<sup>17</sup> but for the purposes of this study,  $\sigma_y$  is defined as the stress at which the transition from a non-steady-state to a steady-state shear rate is observed (see Figure A-11c).<sup>18</sup> Figure 3-5a shows the plot of the plateau modulus and the yield-stress for CFs made from P<sub>1</sub> particles when the particle volume fraction  $\phi_p$  is varied at fixed oil-particle ratio q = 1. The figure shows that the value of  $G_0$  is higher than the value of  $\sigma_y$ , however both

 $G_0$  and  $\sigma_y$  increase with  $\phi_p$ , indicating that the particle network strength in CFs increases with the particle fraction.



Figure 3-5 Plots of rheological changes to the plateau modulus ( $G_0$ : black squares) and yield stress ( $\sigma_y$ : black circles) in the capillary state, when: a) particle volume fraction is varied at fixed oil-particle ratio ( $\varrho$ ) and b) oil-particle ratio is varied at fixed particle fraction ( $\phi_p$ ) of P<sub>1</sub> particles. Gray markers in (b) are for an oil-free foam (Pickering foam).

In Figure 3-5b, we plot the change in modulus and yield stress of CFs prepared with P<sub>1</sub> particles at different oil-particle ratios for  $\phi_p = 1.38$ . The data shows that above some minimum threshold value of  $\rho$  both  $G_0$  and  $\sigma_y$  are insensitive to variations in the oil-particle ratio (and by extension, insensitive to the number of oil droplets in the oil regime explored). This insensitivity of  $G_0$  and  $\sigma_y$  was established for different values of  $\phi_p$  (see Figure A-11a). The only significant change observed in Figure 3-5b is the increase in the values of  $G_0$  and  $\sigma_y$  between  $\rho = 0$  and  $\rho = 0.2$ . This increase in  $G_0$  and  $\sigma_y$  highlights the rheological differences between the Pickering foam (no oil,  $\rho = 0$ ), and the CF formed in the presence of a small amount of oil. Although we observed that the tiny amount of oil

induces sharp rheological changes at different values of  $\phi_p$  used to prepare the CFs, we note that the changes are more prominent as  $\phi_p$  increases. Figure 3-5b shows that once the CF is formed, increasing rho to as much as 1.4 does not affect the rheological properties of the CF. In fact, the raw data of the FS and flow curves, from which the values of  $G_0$  and  $\sigma_y$  in Figure 3-5b were extracted, collapse onto each other, showing that both the values of  $G_0$  and  $\sigma_y$  are independent of  $\varrho$  for a given value of  $\phi_p$  (see Figure A-11b&c).

# 3.3.2.1 Effect of Particle Wettability on Capillary Foam Rheology

Apart from the changes in the microstructure of CFs, we observed that the particle wettability also affects the rheology of CFs. To show the effects of particle wettability on CF rheology, the values of  $\sigma_y$  and  $G_0$ , obtained when the particle volume fraction is varied in CFs made from either P<sub>1</sub> particles (capillary state) or P<sub>2</sub> particles (pendular state), are compared in Figure 3-6a.



Figure 3-6 (a) Comparison of plateau modulus ( $G_0$ : squares) and yield stress ( $\sigma_y$ : circles) of capillary foams made with P<sub>1</sub> particles (solid symbols: capillary state) and

 $P_2$  particles (open symbols: pendular state). (b) Plot of the modulus (squares) and yield stress (circles) in CFs made from  $P_2$  particles at varying oil-particle ratio when  $\phi_p = 0.92$  %. Gray markers in (b) are for the oil-free Pickering foam. Inserting data for the capillary state in (b) for a direct comparison would compromise the clarity of the figure, but such comparative data can be found in Figure A-12a.

Figure 3-6a shows that CFs in the pendular state have higher values for both  $\sigma_y$  and  $G_0$  in comparison to CFs in the capillary state. The moduli of the CFs in the pendular state are almost double the moduli in the capillary state ( $G_{0, pend} \sim 2G_{0, cap}$ ), while the yield stress of the CFs, although more similar in both states, are still higher in the pendular state. The observation that the pendular state is associated with a higher network strength than the capillary state may be rationalized by noting that the network-strengthening interparticle force mediated by the oil bridges contains two contributions: a contribution from the meniscus interfacial tension that is always attractive between two particles of equal wettability, and a contribution from the Laplace pressure that is also attractive in the case of concave bridges (pendular state) but repulsive in the case of convex bridges (capillary state). For a more quantitative description, we refer to the excellent historical perspective article by Danov et al.<sup>19</sup>

When the oil-particle ratio is varied between  $0 \le \varrho \le 1.8$ , at a constant volume fraction of P<sub>2</sub> ( $\phi_p = 0.92$  vol. %), we observe that both  $\sigma_y$  and  $G_0$  increase initially for  $0 \le \varrho \le 0.2$ , peak at  $\varrho = 0.2$ , and then slightly decrease beyond  $\varrho > 0.2$  (see Figure 3-6b). The rheology data on CFs in the pendular state bolsters the initial observation that increasing the oil concentration, over a wide range of oil-particle ratios, has little effect on the rheological properties of CFs. We expect however that at very high concentrations of oil, there will be significant decreases in  $\sigma_y$  and  $G_0$  of CFs as the strength of the oil bridges between the particles weaken due to the presence of large oil droplets disturbing the continuity of the particle network. It is also worth noting, in Figure 3-7, that the CFs made from P<sub>3</sub> exhibit the highest  $G_{\theta}$  and  $\sigma_y$ , of all the particles used in this work; this confirms the dual effect of the particle wettability on the both the state of the particle network and the rheology of CFs. The plot shows that both the plateau moduli and yield stresses increase as the particle wettability shifts towards favorable wetting of the secondary fluid (oil) in CFs. The rheology data shows that the type of bridging in the particle network quantitively affects the values of  $G_{\theta}$  and  $\sigma_y$ , but does not alter the qualitative dependence of rheological properties on the oil and particle concentrations.



Figure 3-7 Plot of the plateau modulus versus yield stress in capillary foams made from: P<sub>1</sub> particles (black square), P<sub>2</sub> particles (red circle), and P<sub>3</sub> particles (blue diamond) when  $\phi_p = 0.92$  vol.% and  $\varrho = 1$ 

The effect of the particle wettability on the values of  $G_0$  and  $\sigma_y$  in CFs is not so surprising, as we have previously explained, in Chapter 2, that the particle network significantly contributes to the rheology of CFs. The results here show that the gel network in CFs becomes stronger as the particle wettability shifts towards the secondary liquid. The increase in  $\sigma_v$  and  $G_0$  values likely results from the observed differences in the foam microstructure. Bossler et al. showed that in capillary suspensions, the formation of pendular bridges leads to stronger gel network than the bridging of multiple particles typical of networks in the capillary state.<sup>20</sup> Yang et al. also observed a decrease in the storage modulus in capillary suspensions as the particles become less wetted by the minority liquid.<sup>21</sup> Shifting the particle wettability away from the secondary liquid precludes the formation of pairwise concave bridges between particles in the gel network because the system energy is minimized by particles clustering around droplets of the secondary liquid. Although particle clusters are more prominent in the capillary state, Bindgen et al. observed that increasing the oil concentration also led to the occurrence of some particle clusters in pendular state networks.<sup>22</sup> That study established that the increase in particle clusters correlates with a reduced  $G_0$  even in the pendular state of capillary suspensions. The results of Bindgen's work are consistent with the results of Bossler and Yang and shed light on the effects of wettability on particle clustering and the rheology of capillary suspensions.

In capillary foams the rheological differences between the pendular and capillary network states are less pronounced than in capillary suspensions. In capillary suspension, the values of  $G_0$  and  $\sigma_y$  are hundreds to thousands of Pascals lower in the capillary state than in the pendular state.<sup>23</sup> By comparison, the values of  $G_0$  and  $\sigma_y$  in both states in CFs only differ by tens to hundreds of Pascals. This significant reduction in the effect of particle wettability on the rheology stems from the presence of bubbles in CFs and the fact that the particle network occupies a lower volume fraction in CFs than in capillary suspensions. While it is known that the bubbles and the particle network both contribute to CF rheology, their contributions are difficult to separate. Another reason capillary suspension rheology depends sensitively on the network type is because the network dictates how the secondary liquid is incorporated into the network. The rheology of capillary suspensions is sensitive to excess secondary liquid, which has been shown to weaken the network strength. Capillary foams, by contrast, are less sensitive to weakening by excess oil, because here the oil can be partly sequestered in the bubble coats where it does not hurt the network strength.

The micrographs in Figure 3-1, Figure 3-2, and Figure 3-3 show that the presence of oil droplets in CFs depends on the particle wettability and is a function of  $\rho$ . We note, however, that the droplets of excess oil do not have a significant effect on the plateau modulus and yield stress: at a fixed particle wettability, both properties hardly change with  $\rho$ . In both network types, the oil in CFs primarily coats the bubbles and bridges the particles and only exists secondarily as droplets in the particle network. Although the number of droplets and the droplet sizes increase with the oil concentration, the overall oil content never exceeds 3% of the CF volume, and as such the oil droplets do not significantly contribute to the CF rheology. We believe that the effects of oil saturation on CF rheology are mitigated by the dominance of the capillary forces exerted by the bubbles and the droplets.

# 3.3.3 Foamability

The particle network in CFs, as seen above, is intimately connected to the foam rheology, but also responsible for the retention of air bubbles within the foam.<sup>7</sup> Foamability

in CFs depends on the formation of oil-bridges between the particles and particle-assisted spreading of oil around gas bubbles. Therefore, we studied how the network type and oil content affect the total amount of air retained in the resulting foam. Here, CFs were prepared at different volume fractions of particles with different wettability while keeping  $\rho$  constant, and at different oil-particle ratios while keeping  $\phi_p$  constant. The foam volume and the gas volume fraction ('foam quality') of the CFs produced were quantified to understand the effects of  $\phi_p$ ,  $\rho$ , and wettability on foamability. The foam volume was determined by measuring the height of the foam head in a cylindrical vial with known radius. The foam quality was determined according to Equation 3-1

Foam Quality 
$$(\phi_g) = \frac{\text{Foam volume-volume of (particle suspension+oil)}}{\text{Foam Volume}}$$
 (3-1)

Once the CFs were prepared, the foam volume and quality were monitored for 2 h; no significant changes with time were observed following the first hour, we therefore consider and call the foam volume at this stage "final". Figure 3-8a and b show the respective values of the initial foam volume and final foam quality of CFs in the pendular and capillary states when  $\phi_p$  is varied at a constant oil-particle ratio of  $\varrho = 1$ .



Figure 3-8 Plots of a) capillary foam volume and b) foam quality as a function of particle volume fraction  $(\phi_p)$ . Plots of c) capillary foam volume and d) foam quality as a function of oil-particle ratio  $(\varrho)$ . The estimated typical uncertainty, indicated for just a few representative data points, results primarily from accuracy limitations in measuring the foam height.

Figure 3-8a shows that the values of the initial foam volumes of CFs in both network states follow a similar trend; both values of the foam volume initially increase with  $\phi_p$  and then decrease at higher values of  $\phi_p$ . Note however, that the maxima for the initial foam volume plots are different; while the initial foam volume in the capillary state starts to decrease at  $\phi_p \approx 0.7$  vol. %, the initial foam volume in the pendular state does not start to decrease until  $\phi_p \approx 1$  vol. % and does not decrease as much as the foam volume in capillary state. The plots of initial foam quality for both states follow the same nonmonotonic trend as the plots of the initial foam volume (Figure A-15 and Figure A-16): the initial foam quality increases with  $\phi_p$  and then decreases as  $\phi_p$  increases further. Figure 3-8b highlights the *final* foam quality obtained after 2 h. This final foam quality decreases monotonically as a function of  $\phi_p$  for foams both in the pendular and in capillary states.

The observed dependence of rheological properties like  $G_0$  on  $\phi_p$  can help explain some of the foamability results in CFs. The CF volume and quality plots reveal that the initial foam volume is determined by the volume of gas incorporated into the foam matrix and is connected to the strength of the gel network entrapping the gas bubbles. To entrap gas in a viscoelastic medium, the bubbles need to be generated via frothing, and immobilized within the medium. We suspect that the strength of the medium works against bubble generation, since generating a bubble requires major deformation of the medium. As  $\phi_p$  increases, rigidity in the particle network increases, thus making bubble generation more challenging in CFs. Figure 3-8b shows that the volume of gas incorporated into CFs linearly decreases with increasing  $\phi_p$ , which correlates with an increase in  $G_0$ , and thus suggests that the strength of the particle network plays a role in determining the volume of air incorporated into the CF. As previously reported for ternary fluid/fluid/particle systems, where one of the fluids is air, the system "decides" how much air is entrained.<sup>6</sup> While the bubble interface in ternary systems is stabilized solely by particles, CFs additionally require oil to coat the bubbles.

Figure 3-8c and d show the initial foam volume and final foam quality plots for CFs produced when varying  $\rho$  at constant  $\phi_p = 0.92$  vol. %. The foam volume and foam quality plots in the capillary state show that an initial increase in *q* results in an increase in both initial foam volume and final foam quality. In the pendular state however, the foam volume and quality of the CFs formed are insensitive to the oil content for  $\rho \ge 0.2$ . It is important to note that when increasing  $\rho$ , the oil volume added to the mixture used to prepare the CFs does not account for the increase in CF volume observed in Figure 3-8c. In fact, the total increase in the oil concentration is  $\sim 100 \ \mu l$ , whereas the foam volume increase is several milliliters. Moreover, the addition of a miniscule amount of oil (~12  $\mu l$ ), to increase  $\rho$  from 0 to 0.2, not only enables the creation of a capillary foam rather than a Pickering foam (oilfree, particle stabilized foam), but also leads to a considerable increase (>10 vol. %) in the volume of gas incorporated into the CF matrix, see Figure 3-8c. The range of gas fractions  $(0.3 \leq \phi_g \leq 0.45)$  obtained from volumetric analysis in Equation 3-1 is also observed to closely agree with the fraction of bubbles estimated from the confocal micrographs. For example, confocal micrographs in Figure 3-2a and Figure 3-3a suggest that the foam quality of CFs, at  $\rho = 0.2$ , is higher in the pendular state than in the capillary state. The values in Figure 3-8d, at  $\rho = 0.2$ , confirm that the foam quality in the pendular state at  $\sim 40\%$  is higher than the foam quality in the capillary state at  $\sim 30\%$ . Given the trends observed in how the foam volume, foam quality and microstructure change with  $\rho$  for both pendular and capillary states, we better understand how the bubbles in CFs can act as reservoir for oil. When the oil content of a CF in the capillary state is increased, that oil can go towards the bubble coats, but the particle network can also absorb more oil, forming more large bridges connecting multiple particles, and it can more readily accommodate

droplets of bulk oil (bright spots in micrographs) because the particles have the right wettability to stabilize O/W emulsion droplets. In contrast, the oil content in the particle network of pendular state CFs does not easily grow by incorporating large oil bridges or particle-stabilized droplets. Rather, the excess oil in pendular state foams goes primarily into bubble coats, and the foam volume and quality are insensitive to the oil content.

#### 3.3.4 Short Term Foam Stability

The volume of CFs was measured at different time points within the 2 h experimental time to determine the relative foam volume changes and thereby quantify the short-term stability of the prepared CFs at different particle volume fractions and oil-particle ratios. In Figure 3-9a and b, we plot the volume evolution of foams in the capillary state (normalized by their respective initial values shown in Figure 3-8a and c). The same qualitative trends in the foam evolution with varying  $\phi_p$  and  $\rho$  seen in Figure 3-9 were also found for in pendular state foams (see Figure A-17a). The loss of volume monitored here is primarily due to water drainage from the foam head.



Figure 3-9 Plot of relative volume change with time in CFs prepared with P1 particles (capillary state) when a) oil-particle ratio ( $\varrho$ ) and b) particle volume fraction ( $\phi_p$ ) are varied. Data for the Pickering foam ( $\varrho = 0$ ) in (a) are depicted by gray open markers

Inspection of both plots in Figure 3-9 shows that  $\phi_p$  has a stronger influence than  $\rho$  on the change in the volume of CFs. In fact, a closer look at Figure 3-9a shows that foam stability is essentially independent of  $\rho$  as long as a minimum amount of oil is present. All the data for CFs at different non-zero oil-particle ratios follow a similar trend and fall onto a single curve. A master curve for the CF stability at this  $\phi_p$  can be expressed by an exponential foam decay from the initial volume  $V_o$  to the final volume  $V_{\infty}$ ; *i. e.*, the relative volume follows  $\frac{V(t)}{V_o} = \frac{V_{\infty}}{V_o} + \left(1 - \frac{V_{\infty}}{V_o}\right)e^{-t/\tau}$  with characteristic decay time  $\tau = 19$  min for the capillary state (dashed line in Figure 3-9a) and  $\tau = 7.0$  min for the pendular state. In a similar experiment where  $\rho$  was varied at  $\phi_p = 1.38$  vol. %,  $\rho$  was also found have no effect on the relative volume fraction (see Figure A-17b). Note that the relative volume change with time for the Pickering foam ( $\rho = 0$ ), does not fall onto the master curve (see open triangles

in Figure 3-9a). This highlights a stability difference between capillary foams and Pickering foams and shows that the presence of even a little bit of oil impacts foam stability in this system.

Figure 3-9b shows that the particle volume fraction  $(\phi_p)$  strongly affects the stability of CFs in time. The plots show that the retained foam volume increases with the particle volume fraction in the CF. Note that even at the highest volume fraction of particles tested,  $\phi_p = 1.76$  vol.%, the foam volume still decreases slightly with time. The data in Figure 3-9b also suggests two stability regimes: for  $\phi_p < 1.38$  vol.%, the foam stability over time is sensitive to changes in  $\phi_p$ , whereas for  $\phi_p \ge 1.38$  the foam stability becomes insensitive to  $\phi_p$ .

The strength of the particle network also influences the stability of CFs over time. Figure 3-9b shows that drainage over time in CFs reduces as  $\phi_p$  increases. Strengthening the particle network, by increasing  $\phi_p$ , arrests and significantly reduces drainage in CFs. We suspect that as network strength increases, more bubbles and particles are connected and held tightly within the CF network. We see that once the foam is formed, a stronger medium favors foam stability.

In summary, we have seen that although the particle network in CFs is mediated by both the oil and particles, it is the particle volume fraction and not the volume of oil that mostly controls the network strength in CFs (Figure 3-5 and Figure 3-6). The particle network strength influences the volume of air generated and retained in CFs (Figure 3-8b and Figure 3-9b). At low network strength it is easy to generate bubbles, but foam stability is poor because of the lower gel strength of the medium. In contrast, CF stability

increases with network strength whereas foamability decreases because the medium is not easily deformed at high network strength. Furthermore, we have seen that both  $G_0$  and foam stability in CFs are insensitive to the volume of oil at constant  $\phi_p$  (Figure 3-5b and Figure 3-9a) and that without the oil,  $G_0$  decreases, and the Pickering foam produced is less stable than the CF. The finding that  $\phi_p$  mainly controls the modulus in CFs, is in stark contrast to what has been observed in previous research on capillary suspensions, the gas-free analogues of our CFs.<sup>15, 24</sup> It has been shown that increasing  $\phi_p$ results in a higher elastic modulus (G) in capillary suspensions.<sup>14, 25</sup> Increasing  $\rho$  from 0 to  $\rho = 0.2$ , increases G; however, for  $\rho > 0.2$ , the value of G decreases for capillary suspensions in the pendular state. The work on capillary suspensions points to the fact that the maximum strength of the gel particle network is achieved around  $\varrho \cong 0.2$ , and that further addition of secondary liquid beyond this point is detrimental to the strength of the particle network.<sup>22, 24</sup> In CFs, by contrast, the additional secondary liquid (excess oil) hardly affects the network strength, but can be beneficial to foamability. CF volume and quality in the capillary state increase with  $\rho$  (Figure 3-8c and d), whereas both  $G_0$  and  $\sigma_y$ are insensitive to  $\varrho$ . We thus find that foamability in CFs is determined by both  $\phi_p$  and  $\varrho$ . The data from this study suggests that additional oil helps to stabilize newly formed bubbles, thereby increasing the volume of gas incorporated into CFs. Furthermore, we see that the excess oil does not significantly affect the rheology and stability of CFs and can promote foamability.

## 3.4 Conclusion

We have investigated how varying the wettability and concentrations of oil and particles in capillary foams (CFs) can influence properties such as the microstructure and rheology of CFs. By performing microscopy, rheology, and foaming experiments, we determine how the structure of the particle network, the size of the foam head, and the rheological properties of yield stress and storage modulus in CFs depend on the volume fraction of particles, the concentration of oil, and the particle wettability.

Confocal microscopy images of CFs highlight the foam's microstructure and document, for the first time, the inclusion of oil droplets in CFs. We observed that the particle wettability influences the rheology and the presence of droplets in the CF microstructure. The rheology results show that particle volume fraction ( $\phi_p$ ) controls gel strength in CFs. We see that both the yield stress ( $\sigma_y$ ) and plateau modulus ( $G_0$ ) in CFs are primarily controlled by  $\phi_p$  and rather insensitive to the oil concentration because much of the excess oil in CFs can partition into the bubble coats. Consequently, the foam stability, which correlates with the gel strength, is also fairly insensitive to variations in the oil content but improves with increasing particle volume fraction. The dependencies for foamability by contrast, are more complicated because the nascent gel network formed in the frothing process has the antagonistic effects of making bubble generation harder and bubble retention easier. These observations support the notion that the gel strength determines both foamability and stability in CFs, that CF properties are oil tolerant and can be tailored to meet specific application demands.

The results of this work not only extend our knowledge of CFs but also help to better understand how CFs differ from ternary systems and provide a starting point for developing new commercial foam products and engineering CFs for use in industrial processes, an example of which could be enhanced oil recovery.

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# CHAPTER 4. DYNAMICS AND AGING OF CAPILLARY FOAMS

## 4.1 Introduction

In many foam-containing products and processes, foams are set in motion by applying a stress; if the applied stress is below the yield stress, the foam can flow in a plug via slip at the wall. However, if the applied stress is above the yield stress, steady shear flow sets in, causing bubbles to slide past each other and liquid to be displaced from the plateau borders and thin films.<sup>1-2</sup> The benefits of flowing foams can be observed in applications such as firefighting where foams are used to suppress combustion, in oil recovery where foams help to displace oil trapped in reservoirs, and in household/cosmetic products where foams aid delivery of active ingredients.<sup>3-4</sup> Foam performance in many of such applications is determined by the stabilization mechanism as well as the interdependent dynamic processes of coarsening and drainage that govern the liquid fraction and bubbles sizes, which in turn affect the properties of the foam during use.<sup>5</sup> Fundamental understanding of foam dynamics can thus help in effectively engineering foam properties for different applications.<sup>6</sup>

Although the rheological studies in Chapters 2 and 3 provide the foundation for understanding CFs properties, for more practical purposes, it is useful to observe CF dynamics under pressure driven flow, as is the case in many applications. For example, the high viscosity, long-term stability, and oil resistance of CFs suggest that they could potentially be useful as a displacing fluid in enhanced oil recovery (EOR) where oil-stable foams are required to efficiently displace oil. However, to explore the efficacy of CFs in applications such as EOR, flow experiments can be conducted to assess how gravity, capillary, viscous and inertial forces influence CF dynamics and stability. In addition, CF flow observations could provide answers to salient questions regarding the influence of the oil coating on gas diffusion between bubbles and conditions at which the particle network immobilizes bubbles and liquid under gravitational and viscous forces. The answers to questions on CF flow and aging dynamics provide understanding on how to engineer CFs for applications in various products and processes.

In this chapter, we study the dynamics of capillary foams through visual observations of the foam flow, and analysis of CF aging and rheology. CF flow through millimeter sized tubing (ID: 790  $\mu$ m) is visualized via microscopy and high-speed imaging. We outline and discuss the stability and mechanics of CFs flowing in tubes. We explain the observed behavior of CFs at investigated flow rates by considering the interdependent rheological and aging properties that influence foam flow. Lastly, we discuss how these results relate to potential use of CFs in microflow applications.

# 4.2 Experimental Section

#### 4.2.1 Materials

Amorphous fumed silica particles modified with dichlorodimethylsilane and containing 50% residual SiOH on the surface were provided by Wacker-Chemie AG (Germany). Particle size and zeta potential were determined by dynamic and electrophoretic light scattering using a Malvern Zetasizer Nano ZS90. The hydrodynamic radius of the above silica particles in 5 mM NaCl solution at pH 4.9 is 403 nm.

Trimethylolpropane trimethacrylate (TMPTMA) and Rhodamine 6G (Fluka) were obtained from Sigma-Aldrich. De-Ionized water was used as the primary aqueous phase. Foams were prepared using a rotor-stator homogenizer (IKA Ultra-Turrax T10, rotor diameter of 6.1 mm, stator diameter 8 mm).

#### 4.2.2 Capillary Foam Preparation

Silica particles were first dispersed in water following the procedure outlined in Chapter 3. Silica particles were suspended in DI-water at different volume fractions and TMPTMA was added to the silica suspension at 1 wt. %. NaCl salt was added to the mixture to achieve a 5 mM concentration. Capillary foams were prepared in a 10 ml BD syringe or 20 ml vial by mechanically frothing the mixture with the IKA Ultra-Turrax at 30,000 rpm for 2 minutes.

# 4.2.3 Foam Flow Experiments

Capillary foams were prepared in a 10 ml BD syringe and were allowed to drain and settle for 30 min. The water at the bottom of the foam was first pushed out by displacing the water with the foam head, which is the more viscous fluid, and then the CFs were pumped through a polytetrafluoroethylene (PTFE) tube (ID: 0.79 mm; OD: 1.58 mm; L: 60 cm) into a collection vessel (20 ml vial) downstream using a KD Scientific (model 210) or a New Era (model 1010) syringe pump as shown in Figure 4-1.



Figure 4-1 Schematic of the set-up used in capillary foam flow and flow imaging experiments (size proportions of the components not to scale).

Before each experiment, the tube was rinsed twice with 5 ml of DI water and the collection vessel was filled with 4 ml of water so that the foams did not dry out. CFs were pumped at flow rates between 0.1 ml/min and 10 ml/min. Foam flow is typically characterized by slip at the wall and as such, all shear rates ( $\dot{\gamma}$ ) and reported in this work are apparent.<sup>7-8</sup> Shear rates reported in foam flow experiments in the tube are determined by dividing the velocity by the tube inner diameter.

# 4.2.4 Foam Imaging Experiments

Capillary foams were imaged using optical light microscopy on an inverted microscope (Nikon, Eclipse TE 2000-E, 10x objective). CF (pumped and unpumped) samples obtained from the middle portion of the foam head were placed in an observation cell and multiple foam images were captured at different time points over a 24 h period.
The average bubble diameter at each time point was obtained by averaging the diameters of at least 200 bubbles from multiple image frames. Foam flow was imaged through the tubing on an upright microscope (Olympus, BX 51, 4x objective). A Phantom V7 high-speed camera was attached to the upright microscope to record foam flow at different flow rates. All microscopy images were processed using ImageJ software while the videos frames were analyzed with home-made MATLAB code.

#### 4.2.5 Rheology Measurements

An Anton Paar MCR 501 rheometer equipped with a temperature controller was used to perform rheological measurements on capillary foams. To prevent inaccuracies that arise from shear localization and wall-slip in rheological measurements, a vane geometry tool (diameter = 16 mm, length = 22 mm) was used in the yield stress measurements. A Couette geometry tool (bob diameter = 26.6 mm, length = 40 mm; cup diameter = 28.9 mm) was used to in controlled strain rate experiments.

The capillary foams were prepared in the Couette cup of the rheometer. The temperature was maintained at 25°C. Once prepared, the CFs were allowed to rest for 10 min before the start of the oscillatory and steady shear experiments. Frequency sweep oscillatory measurements within the linear viscoelastic regime were obtained before and after each experiment to assess the state of the foam.

## 4.3 **Results and Discussion**

#### 4.3.1 Foam Flow

Capillary foams prepared at a particle volume fraction  $\phi_p = 0.68$  vol. % and oilparticle ratio  $\varrho = 1.4$  were pumped through a PTFE capillary tube to observe their stability and determine their characteristics at different flow rates. Macroscopic and microscopic recordings of CFs flowing in the tube provide fundamental understanding on the CF dynamics. The water phase of the CFs *i.e.*, the particle network, was labeled with Rhodamine dye to track CF bubbles, which appear darker than the particle network in Figure 4-2 under florescence excitation in microscopic imaging experiments.



# Figure 4-2 Image of capillary foam under florescence excitation showing the bubbles in the tube.

The flow profile for CFs was obtained in Figure 4-3a by tracking CF bubbles in foam flow experiments with shear rates  $\dot{\gamma} > 10^2 \text{ s}^{-1}$ . The bubbles in the lowest shear rate experiment, when  $\dot{\gamma} \approx 27 \text{ s}^{-1}$ , were not tracked because the flow was not steady.



Figure 4-3 a) Flow profile of capillary foams between  $10^2 < \dot{\gamma} < 10^4 \text{ s}^{-1}$ . b) Capillary foam volume recovered after pumping through the tube at various shear rates ( $\dot{\gamma}$ ). Grey square in (b) corresponds to unsteady flow

Video micrographs show that CFs flow by slipping at the wall of the tube. At most flow rates, the foam maintains either bubble flow or slug flow in the tube. The foam flow profiles obtained in Figure 4-3a, with the exception of  $\dot{\gamma} \approx 2667 \text{ s}^{-1}$ , confirm that the CFs maintain a near plug like flow profile that is typical of yield stress materials. At the lowest flow rate explored, when  $\dot{\gamma} \approx 27 \text{ s}^{-1}$ , the flow starts out as slug flow but becomes more stratified towards the end of the experiment.<sup>9</sup> The CF flow profiles show that significant shearing does not begin until very high shear rates, when  $\dot{\gamma} \ge 10^3 \text{ s}^{-1}$ . At  $\dot{\gamma} \approx 1333 \text{ s}^{-1}$ , a plug regime exists in the center of the tube, however the flow profile shows that light shearing occurs at the edge of the tube. The flow profile for  $\dot{\gamma} \approx 2667 \text{ s}^{-1}$  shows complete shearing of the CFs and suggests yielding of the foam. One of the features observed in micrographs of CFs flowing in a tube is that large bubbles travel in clusters. We suspect that this happens because large bubbles extend into the slow regions of the flow and therefore smaller bubbles in the region behind catch up to the large bubbles. Remarkably, few gas plugs are observed during steady CF flow and we believe that the particle network plays a role in keeping bubbles together in clusters and reducing destruction of large bubbles through coalescence.

The volume of CF collected from the tubing was quantified and compared to the initial foam volume to determine how much of the capillary foam was destroyed during pumping. The percentage of foam volume recovered, relative to the volume of foam prepared, after pumping at different shear rates is shown in Figure 4-3b. The plot shows that CFs can be recovered from pressure driven flow spanning three orders of magnitude of shear rate. For  $\dot{\gamma} > 10^2 \text{ s}^{-1}$ , 90% or more of the CF volume pumped is recovered on average. However, at a low shear rate of  $\dot{\gamma} \approx 27 \text{ s}^{-1}$ , a significantly smaller portion of the foam, compared to the higher shear rates, is recovered.

The uniformly high recovery of CFs at high and intermediate shear rates is surprising given the differences in the flow profile at these different shear rates. We would expect that at the highest shear rate the particle network is stretched or broken, the bubbles are elongated, and the foam collapses. However, comparisons of microscopic images of CFs at different shear rates in Figure 4-4 suggest that CFs remain stable at both the intermediate and high shear rates. At the intermediate shear rates (see Figure 4-4b & c), we observe a large concentration of small and medium size bubbles; additionally, we notice that the density of the particle network around the bubbles at these shear rates prevents the bubbles from being clearly seen. In contrast, at the lowest and highest shear rates, we observe a mixture of large and small sized bubbles (see Figure 4-4a & d respectively) and note that the large bubbles at the highest shear rate are slightly elongated. Given the plug flow profile obtained at the intermediate shear rates, the observed network retention is expected because the foam was not subjected to significant shear. However, the large gas plug observed at the lowest shear rate (Figure 4-4a) indicate CF breakdown that is unexpected when the foam is subjected to less shear than the higher shear rates.



Figure 4-4 Micrographs of capillary foams flowing through the tubing at  $\dot{\gamma} \approx a$ ) 27 s<sup>-1</sup>, b) 133 s<sup>-1</sup>, c) 266 s<sup>-1</sup>, d) 2667 s<sup>-1</sup>.

We characterize CF stability by understanding both bubble stability and network integrity. Network and bubble deformation in CFs likely differ from one another at different stresses. Figure 4-4d indicates that shearing in the CFs leads to the presence of larger bubbles and the breakdown of large particle aggregates. While we do not see clusters of particle aggregates in Figure 4-4d, we observe particle aggregates macroscopically upon recovery of CFs, suggesting the particle network is not destroyed. We note however, it is possible that the particle network is considerably strained or altered by the flow, as the flow profile shows that considerable shearing occurs at the highest shear rate. The observations here suggest that a high percentage of the CF can still be recovered even when the particle network is sheared at the highest strain rates because the bubbles do not phase separate out of the foam by combining to form large gas plugs. Figure 4-4d shows that individual bubbles are preserved even when shear is strong enough to disrupt the network; this is perhaps because the hybrid coat of oil and particles create dense layers and rigid interfaces, that reduce the kinetics of diffusive coarsening and bubble coalescence. The results suggest that, despite physical connections between the particle network and the bubbles, the stability of both appear somewhat independent of each other.

The notion that bubble stability and network integrity are affected differently by shear does not contradict the observations at intermediate shear rates where the data suggests that both bubble stability and particle network integrity are maintained. While this analysis is consistent in explaining the high CF recovery at the higher shear rates, the analysis does not provide a full picture required to explain the CFs behavior at the lowest shear rate ( $\dot{\gamma} \approx 27 \ s^{-1}$ ). To understand the CF behavior in the lowest  $\dot{\gamma}$  regime, the effects of different forces that influence CF flow need to be explored. In addition, the effect of the particle network on bubble stability needs to be understood and the role of bubble stability on the overall CFs stability needs to be made clear. Up unto this point in the discussion on CF flow, we considered that the significant forces acting on the CF are the pressure gradient imposed by the pump and the shear stress. However, as we will see in the following sections, gravity and capillarity forces, as well as CF rheology, need to be considered because they influence stability and yielding in CFs and explain the different dynamics observed in the low  $\dot{\gamma}$  regime.

### 4.3.2 Short Term Foam Stability

Drainage and coarsening of static CFs were studied in the initial hours following CF preparation to understand CF aging through phase separation which we suspect is responsible for the foam volume loss. The stability of CFs made from PVC particles and TMPTMA oil were previously observed over a period of 5 months. Macroscopically, the PVC/TMPTMA CF was shown to be very stable against drainage and coarsening from the time of foam production through the entire observation.<sup>10</sup> In this work, the short-term stability of silica/TMPTMA CFs against drainage was quantified by measuring the changes to the foam volume over time. Given that previous studies showed that the rheology and short-term stability of silica/TMPTMA CFs is strongly dependent on the particle volume and not the volume of the oil,<sup>11</sup> we monitored the changes in the foam volumes of silica/TMPTMA CFs prepared at different particle volume fractions ( $\phi_p$ ). The silica particle concentration is varied between 0.68, 0.92 and 1.38 vol. % and the TMPTMA oil concentration is kept constant at 0.95 vol. %. Figure 4-5a shows the relative change in foam volume over the experimental time for CFs at different particle volume fractions. While the reported changes in foam volume are due to water loss from the foam head, the overall volume of the foam head and water does not change with time.



Figure 4-5 a) Plot of relative foam volume change with time for static capillary foams at different particle volumes ( $\phi_p$ ) and an oil fraction of 0.95 vol. %. Silica/TMPTMA foams (black square, red circles, blue triangles); PVC/TMPTMA foams (orange diamonds). b) Plot of foam quality at different particle volumes of the silica/TMPTMA CFs 3 h after foaming.

The data in Figure 4-5a shows that the high stability previously observed in the PVC/TMPTMA CF is not immediately realized in the silica/TMPTMA CFs used here. Rather, we see that drainage occurs within the first hour after production of the silica CF and afterwards stops; in contrast, the PVC CFs are stable throughout the experiment. We should note however, that the initial foam volume in the silica/TMPTMA CFs is almost twice that of the PVC/TMPTMA CF for the same frothing conditions; despite the higher volume percent and the larger particle sizes of the PVC particles, the PVC/TMPTMA foam volume is lower. Figure 4-5a also shows that for the silica CFs, the relative foam volume change, due to water loss, decreases as the particle volume fraction increases. This observation, we believe, is a result of the increase in strength of the capillary bridges between the bubbles and the particle network. As the particle network strength increases, more water is retained in the CF.

As seen from the capillary foam schematic in Chapter 1, the particle network occupies a significant portion of the foam structure. The estimated gas volume fraction present in the CF is approximately 45% when  $\phi_p = 0.68$  vol.% and the oil-particle ratio  $\rho = 1.4$ . We have previously shown that the strength of the particle network is responsible for limiting both the incorporation of gas during foam preparation (see Figure 4-5b), and the subsequent water drainage from the CF.<sup>11</sup> The particle wettability measured by the three-phase contact angle ( $\theta$ ) and the volume ratio of particles and particle-bridging liquid have been shown to determine the type and strength of bridges obtained in capillary suspensions, which constitute the gel particle network in CFs.<sup>12-14</sup> More details on the role of particle wettability for CFs can be found in Chapter 3.<sup>11</sup> Briefly, a plausible hypothesis for the existence of drainage in the silica CFs is that thermodynamics drives the foam towards a metastable state of higher rigidity; the water loss slows down internal rearrangements in the foam. Invariably, drainage is observed at every particle fraction tested; however, water loss is most pronounced at the lowest particle volume fraction, when  $\phi_p = 0.68$  vol. %, which is the particle volume fraction in CFs used in the foam flow experiments.

In classical surfactant foams (SFs), drainage events are accompanied by diffusive coarsening and both aging processes drive each other.<sup>15</sup> The action of drainage thins the liquid barrier between bubbles and increases the rate of diffusion that results in larger bubble sizes; as smaller bubbles shrink, the rate of drainage also increases because there more space for drainage to occur, which further reduces diffusion length scales for coarsening, and so on.<sup>16</sup> Coarsening in silica/TMPTMA CFs was quantified by measuring the increase in the average bubble sizes over a period of 24 h. The plots in Figure 4-6a

show the normalized average bubble sizes over time for silica/TMPTMA CFs having the same particle volume fractions as those studied in the drainage experiments. We observe that decreasing  $\phi_p$  leads to both a shortened lag time where bubble growth is slow, and an increase in the rate of bubble growth in CFs at later times. A strong similarity is apparent between the two coarsening curves for  $\phi_p \ge 0.92$  % (red circles and blue triangles in Figure 4-6a) and suggests that that the coarsening behavior is insensitive to variations of  $\phi_p$  at high network strengths.



Figure 4-6 a) Normalized average bubble sizes over time for silica/TMPTMA CFs at  $\phi_p = 0.68$  % (black squares),  $\phi_p = 0.92$  % (red circles),  $\phi_p = 1.38$  % (blue triangles). b) Normalized average bubble sizes over time for static CFs (black squares) and pumped CFs (green diamonds) when  $\phi_p = 0.68$  %.

The slopes of the coarsening plots show that the average bubble sizes in CFs slowly increase within the first few hours and then steadily increase over the remaining period of the experiment. The trend in the coarsening plot of CFs, though comparable to the coarsening behavior observed in SFs, displays differences worth noting. First, the time lag in bubble growth is longer for CFs; SFs exhibit a time lag on the order of minutes,<sup>17-18</sup>

whereas the time lag for CFs as observed in Figure 4-6a, is order of hours. The origin of this time lag can be attributed to a balance between drainage and diffusion in the foam. According to Magrabi,<sup>19</sup> bubble growth and foam instability is controlled by drainage during the lag time, and controlled by diffusion during the scaling regime, and both aging processes are balanced at the transition between regimes. The lag time in CFs corresponds to long drainage times (~ 1 h) observed in Figure 4-5a. In addition, we suspect that the composite layer of oil and particles surrounding the bubbles in CFs contributes to "weak coarsening",<sup>15</sup> which slows the drainage controlled dynamics of the lag regime.

Beyond the lag time in the coarsening plot, we also observed a difference in the coarsening time scaling for SFs and CFs. In SFs bubble growth follows a power law scaling  $t^z$ , with  $0.33 \le z \le 0.5$ , where z = 0.33 in the limiting case of wet foams, 0.5 for dry foams and is ~ 0.45 in high quality SFs.<sup>17, 20</sup> In CFs, we observe that  $R/R_o \sim t^z$ , where z = 0.66, 0.43 & 0.5 when  $\phi_p = 0.68$ , 0.92 & 1.38 %, respectively. The z-values at the higher particle loading in CFs parallel those obtained for SFs, however we suspect that the high z-value obtained when  $\phi_p = 0.68$  % in CFs, results from higher diffusion rates and/or bubble coalescence due to poor coverage of the bubble surfaces at this particle loading. When the CFs are examined macroscopically over long periods of time, we observe that the foam becomes coarser and drier. In fact, after a period of ~ 12 h one can visually observe large bubbles in the foam matrix that could not previously be seen with the naked eye (see Figure A-18). Bubble size analysis becomes more difficult and can be misleading after 24 h, because the bubbles are difficult to observe with light microscopy.

Figure 4-6b shows that the coarsening plot for a CF pumped at  $\dot{\gamma} \approx 1330 \text{ s}^{-1}$  contains no lag regime and that, in the scaling regime, the average the bubble sizes increase at a slightly slower rate  $(R/R_o \sim t^{0.5})$  than the bubble sizes in an unpumped CF  $(R/R_o \sim t^{0.66})$ . The average bubble size in pumped CFs plateaus ~ 8 h (10<sup>4</sup> s) after stopping the foam flow and is not observed to grow further within the duration of the experiment. It is interesting to note that the value of the initial average bubble size for both static and pumped CFs are similar in these experiments. However, the data shows that foam flow leads to the onset of bubble growth *i.e.*, shorter lag time. This early bubble growth points to a disruption of the gel particle network between bubbles and/or a compromise of the oil-particle coating that stabilizes the bubbles in CFs. As Figure 4-4d suggests, high flow rates are capable of both stretching the particle network and inducing bubble growth in CFs. We believe that once the particle network is compromised under shear, CF bubbles can grow, during the time of relaxation downstream, until the bubbles reach optimum sizes and sufficient network connections are restored.

The drainage and coarsening experiments show that the silica/TMPTMA CFs undergo initial changes in structure before settling into a metastable state where foam aging kinetics are slower. An important point to note however, is that the aging kinetics is dependent on both the particle network strength, which is a function of  $\phi_p$ , and the shear history of the foam. By controlling  $\phi_p$ , the intermittent aging kinetics of the foam can be reduced at higher particle loading because the strength of the particle network resists changes to the foam structure. In contrast, when the foam is subjected to higher shear rates, aging is accelerated because the particle network is compromised. The superior long-term stability of sheared CFs seems to indicate that sheared CFs may have a stronger gel network

than unsheared CFs. To better understand how the network strength and shear history influence CF aging, we perform rheological measurements on the CFs used here.

#### 4.3.3 Foam Rheology

Silica/TMPTMA CFs were characterized at different particle volume fractions by measuring the storage modulus (G') and the yield stress ( $\sigma_y$ ) in rheology experiments. The values of the storage moduli and yield stress of the CFs are obtained by performing frequency sweep (FS) and controlled stress experiments (CSS), respectively, with a vane tool. We plot in Figure 4-7a, the values of the plateau of the storage modulus (referred to as the "plateau modulus"  $G_0$  from here on) and  $\sigma_y$  at different particle volume fractions.  $G_0$  is a measure of the rigidity of the particle network in CFs while  $\sigma_y$  measures the resistance to flow and indicates the stress at which steady flow is observed in the foam. Although the plot in Figure 4-7a show that the values of both  $\sigma_y$  and  $G_0$  increase with increasing  $\phi_p$ , at all particle fractions tested,  $G_0 > \sigma_y$ . Higher rigidity in the particle network slows down the actions of drainage and coarsening in the CFs and thus explains the reduced aging effects previously observed at higher  $\phi_p$  in CFs.

By comparing the foam volumes (Figure 4-3b &Figure 4-5a) and evolution of average bubble sizes of pumped and unpumped foams (Figure 4-6b), we have seen that pumping CFs through a tube influences CF aging. Further "before and after" pumping comparisons are called for but would require additional invasive handling of the pumped foam (such as foam transfer to a rheometer cell), which could compromise the foam, and all subsequently obtained data. We therefore adopted a viable workaround: mimicking the shear conditions of tube flow in a Couette cell that can subsequently be used for the rheological characterization of foam properties related to the foam structure without additional handling. The Couette geometry, in which the foam is sandwiched between two smooth walls of concentric cylinders, also allows for slip in shear from motion relative to a smooth wall, as is expected in tube flow.



Figure 4-7 a) Plot of plateau modulus G (black squares), and yield stress  $\sigma_y$  (red circles) of CFs at different particle fractions ( $\phi_p$ ) b) Plot of plateau modulus,  $G_{\theta}$ , of

capillary foams at different particle fractions, before (black squares) and after (red circles) controlled shear rate experiment. c) Shear viscosity plots of CFs at  $\phi_p = 0.68$  %, 0.92 % and 1.38 % (black squares, red circles, and blue triangles).

CFs were subjected to controlled shear rate (CSR) experiments in the Couette cell. Frequency sweep measurements were taken before and after the controlled shear rate experiments to determine the effect of shear on the CFs. The values of  $G_0$  obtained from the FS experiments are shown Figure 4-7b. Comparing the initial and final moduli values of CFs subjected to the CSR, we observe an increase in the value of  $G_0$ , which shows that a CF that has been subjected to shear has a higher modulus than an unsheared CF. The observation of higher moduli in sheared CFs indicates that the particle network in the CF can be made stronger by applying additional shear (pumping) after initial CF preparation.

The increased strength in the CF particle network induced by pumping is remarkable and suggests that there are changes that occur in the CF structure during shearing. We believe that shearing of the CFs further drains the primary liquid from the foam and allows for higher connectivity of the particles by the secondary liquid. Additionally, we suspect some of the bubbles are destroyed during shearing, and while their gas may escape, the oil and particles from their bubble coat may be incorporated into the particle network and strengthen it. The increase in the value of  $G_0$  is also consistent with the hypothesis that following the destruction or removal of the bubbles from a CF, the surrounding particle network, which is a capillary suspension, should remain. Capillary suspensions, although more commonly oil based, usually have higher moduli than CFs.<sup>21-</sup> <sup>22</sup> We have previously shown that that our CFs are less rigid than the capillary suspension that forms their continuous phase.<sup>23</sup> Figure 4-7c highlights the viscosity obtained for CFs at different particle volume fractions during the CSR experiment. The plot shows that CFs are shear-thinning. Although the viscosity decreases consistently throughout the plot, we note that the viscosity slightly increases at the highest shear rate accessible and suspect that this could perhaps be due to formation of new bubbles at high shear rates. The shear viscosity plots of the CFs at different particle volume fractions collapse unto a single curve indicating that the CF viscosity is insensitive to the particle volume fraction and the particle network strength in the explored ranges. The master curve for the shear viscosity in Figure 4-7c follows a power law,  $\eta \sim \dot{\gamma}^{-m}$ , with 3 values of m corresponding to different slope regimes at low shear ( $\dot{\gamma} \leq 10^{-2} s^{-1}$ ) m = 0.77, moderate shear ( $10^{-2} \leq \dot{\gamma} \leq 10 s^{-1}$ ) m = 1.1, and high shear ( $\dot{\gamma} \geq 10 s^{-1}$ ) m = 0.68 (see Figure A-14). We suspect that slip plays a role in CF shearing and influences the different m-values obtained here.

The observation that the viscosity is independent of both  $G_0$  and  $\phi_p$  suggests that the particle network is broken when yielding occurs and/or that the CFs flow by slipping on a thin film of fluid at the walls of the Couette cell. Both ideas are plausible and can be explained by the following reasons. The viscosity plots of CFs could be similar because they represent the shear viscosities of foam containing particle suspensions that result from network break up under shear; the viscosities of low-quality foams and particle aggregates, at low concentrations used in this work, are respectively independent of gas volume fractions and have no observable differences.<sup>24-25</sup> Slip could also be a reason for the similarity in the viscosity plots. Slip precludes accurate viscosity measurements and the smooth walls in rotational geometries are known to promote slip in flow of foams and other granular materials.<sup>26</sup> At the end of the CSR experiments, we confirm that the CFs were indeed drained by noting that the bottom of the Couette cup contains mostly water while most of the foam is located at the edges of the Couette bob and cup, where most of the shearing occurs.

The effects of shear on CFs lead to aging of CFs during and after shearing. We observe from rheology studies that pumping (or shearing) of the CFs increases  $G_0$  and further observe that coarsening in pumped CFs begins immediately after pumping plausibly because of increased drainage during shear. It is well known that pumping surfactant foams accelerates foam aging and mostly destroys the foam; foam disintegration occurs because of diffusion driven coarsening that leads to bubble growth and liquid drainage from the interfacial films.<sup>8, 24, 27-28</sup> The particle network in CFs, however, reduces foam destruction during pumping and in the process the network connectivity is increased. In Chapter 1, the increase in the CF modulus was connected to aging observed in time sweep experiments.<sup>23</sup>

The combined results of the short-term stability and rheology studies not only provide better insight on CF flow dynamics but also provide the understanding of how to manage and limit the effects of shear on CFs. To this end we return to our discussion on CF behavior when pumped at low shear rates ( $\dot{\gamma} \approx 27 \text{ s}^{-1}$ ). We believe that the loss of CFs at the lowest shear rate is a result of aging (phase separation of water and gas from the foam) that is further accelerated by the effects of shear. At the low particle fraction, the gel particle strength is the weakest and for this reason, the CF does not retain the primary liquid (water) to a good extent (see Figure 4-5a). Although the foam is initially drained before pumping begins, there is further loss of water from the CF during the experiment. The continual loss of water from the foam makes the foam more brittle to the stress applied by the pressure gradient driving foam flow and allows for the formation of large gas plugs. During the foam flow experiments at the lowest shear rate, we observed that the portion of the CFs closer to the syringe piston were not only drier but also degraded over time. When the CFs closer to the piston passed through the tubing, they were completely phase separated into foam slugs, gas plugs and water with particles (see Figure 4-8).





To verify that phase separation is indeed the cause of the foam volume loss, the effect of strengthening the gel particle network on foam flow at the lowest shear rate was investigated. Figure 4-9a shows the percentage of foam recovered when CFs at different particle volume fractions are pumped at the lowest shear rate. We observe that by doubling the particle volume fraction, from 0.68 to 1.38 vol.%, the percentage of CFs recovered can be increased to 80%, an average increase of about 15% from when the particle network strength is weaker.



Figure 4-9 a) Plot of capillary foam recovered at different particle fractions when pumped at the lowest shear rate  $\dot{\gamma} \approx 27 \text{ s}^{-1}$ . b) Plot comparing foam recovery when CF flow is directed upward (black squares) and downward (red diamonds).

The increase in CFs recovered with increasing particle volume fraction shows that a strong particle network helps to retain water and preserves the foam from phase separating during pumping. While higher particle loadings in CFs were not explored, we believe that the effects of increasing the particle network strength are only beneficial up to a certain point in CF flow. Higher particle loadings are bound to make flow through narrow tubes difficult and require impractically high pressures to mobilize the foam.

Lastly, we considered the stability of CFs when the flow is directed upward against gravity. Here, we invert the syringe pump set-up and drained the CFs in an upward foam flow direction. We quantify the relative foam volume recovered from the upward foam flow protocol and plot the comparative data for the downward foam flow protocol in Figure 4-9b. We see that the trend in the relative CF volume recovered at the varying flow rates for both the upward and downward flow protocol are similar. However, when the relative foam volumes recovered from both the upward and downward flow protocols are compared, we observe that more foam is recovered from the latter than from the former. We explain this observed behavior by looking at the nature of both fluids: Water and CFs. At low shear rates applied, the CF has very high viscosity and in fact behaves more like a rigid solid at low strains (See Figure A-13c), while the viscosity of water is low by comparison. In the downward flow protocol, the displacing fluid is the foam and as such easily displaces the water from the syringe and through the tube. On the other hand, in the upward flow protocol, drained water at the bottom of the syringe has to displace ("push") the foam, a higher viscosity fluid. We believe that the CF is not uniformly displaced by the water in the upward flow protocol but is actually damaged by fingering channels of water that flow through the CF matrix. This behavior, known as viscous fingering, is usually observed between two immiscible fluids when the less viscous fluid is used to displace the more viscous fluid.<sup>29-30</sup> Under these conditions, we suspect that some of the water flows through the CF and by so doing, destroys certain particle bridges and bubbles that are present in the foam. We show, in Figure 4-10, that particles dislodged from the CF can be seen settling at the top of the piston during the experiment when using an upward flow protocol. In addition to viscous fingering, CFs and foams in general, can also be viewed as porous materials that can allow for flow of liquid through their matrices. Hence water can flow through the foam and can damage the network structure that holds the foam together.



Figure 4-10 Image showing particles dislodged from capillary foam network settling at the top of the syringe piston.

The results of our experiments prove that CFs maintain their stability and rigidity under flow at small length scales (micro flows: < 1 mm). The high viscosity and plug flow profile observed in the CF flow suggest that CFs could be useful as displacing fluids in foam flow applications like sclerotherapy,<sup>28</sup> enhanced oil recovery,<sup>31</sup> or soil remediation.<sup>32</sup> Foam sclerotherapy, for example, involves flowing foam through sclerotic veins in the body to expel all the blood from them, ideally without mixing (*i.e.* via plug flow). Uniform foam propagation and good foam stability in contact with oil would also be beneficial for foam flooding in oil recovery and soil remediation. Still, more research and development will be necessary before CFs can be applied successfully toward any industrial goal.

# 4.4 Conclusion

We have investigated the dynamics of novel capillary foams (CFs) at different flow rates in a small tube with sub-millimeter diameter. Using light microscopy to observe the flow of CFs through the tube, we were able to trace the flow profile and understand how varying degrees of shear affect both the particle network and the oil-coated bubbles in CFs. We also show in this work how aging and foam rheology influences the volume of capillary foams recovered after the foam is pumped through tubing.

Our results show high recovery of CFs when the foams are pumped at intermediate and high shear rates and a lower foam recovery at the lowest shear rate explored. Microscopy images reveal that many of the bubbles are still entrapped by the network at intermediate shear rates, while at higher shear rates the particle network is broken, and large bubbles can be observed. Aging studies show that the strength of the particle network is largely responsible for the observed dynamics of CFs, especially at the lowest shear rate. Aging in CFs can be controlled by tuning the strength of the gel particle network through varying the particle volume fraction. The highest particle volume fraction explored corresponds to the highest gel strength observed, and in this case the amount of foam recovered at the lowest shear rate reaches 80 %. We also observe that pumping the CF through the tubing limits subsequent coarsening. This behavior, we believe, results from the strengthening of the CF particle network when the foam is sheared. Frequency sweep and controlled shear rate experiments corroborate this hypothesis by showing that the elastic modulus of CFs increases after shearing. The strengthening of the CFs occurs because of water and bubble losses that take place during shearing and make the CF more akin to a capillary suspension.

The observed dynamics together with previous rheological studies on CFs suggest that CFs could be useful as displacing fluids for enhanced oil recovery (EOR) and other applications, but more detailed feasibility studies in porous environments are clearly needed.

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# CHAPTER 5. BUBBLE-PARTICLE DYNAMICS IN MULTIPHASE FLOW OF CAPILLARY FOAMS IN A POROUS MICROMODEL

## 5.1 Introduction

The previous chapter on CF flow properties suggest that CFs could function as a displacing fluid in oil recovery applications because its foam architecture affords high viscosity and stability under stress. The fundamental flow properties of capillary foams (CFs) were probed in rheology and foam flow experiments to understand how CFs respond under stress.<sup>1</sup> The observed CF properties such as yield stress, viscosity, stability and tunability could prove advantageous in industrial products and processes.<sup>1-3</sup> For example, enhanced oil recovery (EOR) is an industrial process of interest where the benefits of CF flow properties can be advantageous and leveraged to improve oil yields from underground reservoirs.

Much research has been devoted to probe the pore scale displacement dynamics of foams for EOR and other transport applications in porous media.<sup>4-6</sup> The observations from surfactant and particle-stabilized foam displacement studies, conducted in sandpack, glass, polydimethylsiloxane (PDMS) templated and 3D printed micromodels, not only indicate phenomena that occur in underground pores but also provide insights that improve and aid oil displacement from reservoirs.<sup>7-9</sup> For example, recent foam flooding studies in an oil-wetted heterogeneous porous media revealed three zones that display different foam mechanics: the displacement front, where foam coalesces on initial contact with oil; the

transition zone, where wettability of the medium changes from oil-wet to water-wet; and the foam bank, where foam is generated in the porous medium.<sup>10</sup> In another study, high quality foams were observed to be less stable in the presence of oil and more susceptible to collapse, which thus reduces oil displacement efficiency due to delays in generation and propagation of stable foams.<sup>11</sup> The above highlighted findings, along with other fluid dynamic studies in porous micromodels, contribute to the understanding of multiphase interactions at the pore scale level.<sup>12-17</sup> Although the dynamics of foams and their ability to displace oil from porous media has been extensively studied, the pore scale dynamics of a quaternary-phase colloidal system like CFs has not been reported. There are also, to our knowledge, few existing studies that detail the pore scale behavior of low-quality foams, an example of which includes colloidal gas aphrons.<sup>18</sup>

The structural differences in CFs, *i.e.*, the presence of dual fluid interfaces and a network of particles, are likely to increase the complexity of the dynamics and change the displacement characteristics of foams at the pore scale. Thus, it is important to understand the benefits and practicality of applying CFs in EOR through micromodel studies like those conducted on SFs. Fundamental micromodel studies of CFs will answer questions on how the particle network and observed bubble rigidity in CFs influence clogging, foam propagation, and bubble breakup frequency. In addition, studies on surfactant foams have found no correlation between bulk scale foam stability in the presence of oil and oil displacement efficiency in pores.<sup>19</sup> However, displacement experiments can reveal how the oil-tolerance in CFs influences oil displacement.

In this chapter, we study the dynamics of capillary foams flowing through a PDMS templated micromodel by using high speed video microscopy to probe and record the mechanics of bubbles and particles in CFs at the pore length scale. We outline and discuss capillary foam stability and mobility in the pores and evaluate CF displacement of crude oil from the micromodel. The observed bubble and particle interactions, pore clogging and unclogging mechanisms, and bubble dynamics are highlighted and explained. Lastly, we compare the oil displacement capacity of CF flooding to water and surfactant foam flooding by considering the sweep efficiency, a metric that is important for enhanced oil recovery.

## 5.2 Experimental Section

#### 5.2.1 Materials

Amorphous fumed silica particles modified with dichlorodimethylsilane and containing 50% residual SiOH on the surface were provided by Wacker-Chemie. Particle size and zeta potential were determined by dynamic and electrophoretic light scattering using a Malvern Zetasizer Nano ZS90. The hydrodynamic radius of the silica particles in 5 mM NaCl solution at pH 4.9 is 403 nm. Trimethylolpropane trimethacrylate (TMPTMA) and tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane were obtained from Sigma-Aldrich. Crude oil was obtained from Texas Raw Crude. Deionized water was used as the primary aqueous phase. CFs were prepared using a rotor-stator homogenizer (IKA Ultra-Turrax T10, rotor diameter of 6.1 mm, stator diameter 8 mm).

## 5.2.2 Capillary Foam Preparation

Silica particles were first dispersed in methanol following the procedure highlighted in Section 3.2.2. Silica particles suspended at 1.5 wt. % in Di-Water containing

5 mM NaCl salt were prepared in a 10 ml BD syringe. TMPTMA (1 wt. %) was added to silica suspension. Capillary foams were prepared by mechanically frothing the mixture at 30,000 rpm for 2 minutes.

#### 5.2.3 Design and Fabrication of Micromodel

Device fabrication was performed using conventional soft lithography techniques.<sup>20</sup> The master was fabricated by spin coating two SU8-photoresist layers on a silicon wafer. The first layer (15 um, SU8-2015) was used as an adhesion layer. The second layer (80 um, SU8-2050) was used for molding the microfluidic channels via optical lithography. After development, the master was coated overnight with an anti-adhesive (tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane). A mixture of 10:1 PDMS/ crosslinker was poured on top of the master and left for curing 2 h in a 90 °C oven. Afterwards, PDMS slabs were cut off for each individual network and access wells were punched using biopsy punchers (1 mm diameter puncher for the inlets and 5 mm diameter puncher for the outlet). Finally, each PDMS block was covalently bonded to a glass slide via plasma treatment that oxidizes the silanol groups at the surface.



Figure 5-1 Image showing the micromodel template used to mimic a porous environment

Diameter of	Pore Size	Porosity	Permeability	Pore Volume	Wettability
Post (µm)	(µm)	(%)	(Darcy)	(µl)	
200	100	29	166	0.47	Hydrophobic

Table 5-1 Properties of the micromodel used in capillary foam flow experiments

## 5.2.4 Foam Flow Experiments

Capillary foams prepared in 10 ml BD syringe and were allowed to drain and settle for 20 min. The water at the bottom of the foam was first removed and then the CFs were pumped through a polyethylene (PE) tubing (inner diameter: 0.86 mm; outer diameter: 1.32mm) or a silicon tubing (inner diameter: 0.78 mm; outer diameter: 2.36 mm) into a PDMS templated micromodel using a New Era (model 1010) syringe pump as shown in Figure 5-2. The pressure upstream and downstream of the micromodel was monitored via 30 psi serial sensors (Honeywell, model: 24PCDFG6G). The sensors were connected to homemade board circuits including two-op-amp amplifiers (Texas Instrument, INA126) and various resistors to adjust the gain. The read-out was performed via an Arduino system (chipKIT uC32 Arduino – programmable PIC32 Microcontroller board, Digilent) and a home-made LabVIEW interface. The effluent from the micromodel was collected downstream in a 20 ml vial. New PDMS devices were used for each experiment and the device was degassed and filled with water at the beginning of every experiment except otherwise stated. Shear rates ( $\dot{\gamma}$ ) reported here, as explained in chapter 4, are apparent.



Figure 5-2 Schematic of set-up used to image capillary foam flow and oil displacement experiments (size proportions of the components not to scale).

# 5.2.5 Oil Displacement Experiments

The micromodel was filled with crude oil and allowed to settle for 24 h before the start of the displacement experiments. Capillary foams were prepared, drained, and pumped as described in Section 5.2.4. The displacing fluid *i.e.*, CF or water, was pumped into the micromodel at 0.2 ml/min. CFs pumped into the micromodel were further drained through the drain port for a few minutes, after which CF flow was diverted into the pore space by closing the drain port. The effluent from the device was collected downstream in a 20 ml vial. Repeats of each experiment were conducted with new micromodels.

#### 5.2.6 Foam Imaging Experiments

Capillary foams flowing through the porous environment were imaged using optical light microscopy on an upright stereo microscope (Leica, Model MDG36, 3x magnification). A Phantom V7 high-speed camera was attached to the microscope to record foam behavior at 4000 fps. A CMOS camera (Thor Labs, DCC1645c-HQ) was used to record oil displacement from the micromodel.

## 5.2.7 Image Processing

Microscopy images were processed and colored using ImageJ and Adobe Photoshop software. Videos were analyzed using home-made MATLAB programs. Briefly, bubble information (e.g., number, size, position) was extracted from binary images obtained via simple thresholding. Clogged areas were determined by thresholding the variance of pixel intensity over a 10-frame sliding window at 30 fps.

## 5.3 Results and Discussion

#### 5.3.1 Foam Flow and Stability

Capillary foams pumped through the PDMS templated micromodel were observed to maintain relative foam stability and mobility at varying flow rates ( $\dot{v}$ ). Images and foam volume measurements of capillary foams recovered downstream of the micromodel were collected and are shown in Figure 5-3 below. Figure 5-3a shows the image comparison between an unpumped CF, a CF that was recovered from the micromodel when pumped at  $\dot{v} = 0.8$  ml/min and a CF that was recovered at  $\dot{v} = 0.1$  ml/min. The percentage of foam volume recovered relative to the foam volume pumped into the device at each flow rate was also quantified and is shown in Figure 5-3b. The images and the plot in Figure 5-3 show that CF stability through the porous and tortuous path of the micromodel is influenced by the speed of mobilization and that foam flow at higher speeds enables higher retention of the macroscopic structure in CFs.





Although CFs can progress through the pore spaces, Figure 5-3b shows that more CFs are recovered at the high and intermediate flow rates than at the low flow rate  $(\dot{v} = 0.1 \text{ ml/min})$ . The trend of increased CF recovery and stability at higher flow rates was observed in flow of CFs through tubes in the previous chapter where it was noted that

at the imposed low flow rates, stress hastens CF aging and leads to CF loss over time due to phase separation. Similarly, at low flow rates in this study, segregated regions of gas plugs, water, and foams can be seen (see Figure A-20) flowing into the micromodel. Clogging, which occurs more at lower flow rates, also amplifies the damage done to the CF by facilitating flow of water through the foam matrix in a process reminiscent of viscous fingering. While viscous fingering traditionally involves two immiscible fluids flowing, in CFs, the water flowing through the CF matrix is an integral component of the foam. The observed foam stability and recovered foam volume when CFs flow through tubes (chapter 4) and through the micromodel here, do not differ and thus suggest that porous environments minimally distort CFs. The recovery of CFs from the porous environment underscores the robustness of the foam stabilization mechanism in CFs.

Given the intricate foam architecture and network connectivity in CFs, it was expected that the particle network would clog the pores and prevent the foam flow through the medium or that phase separation will occur due to breakdown of the particle network as the foam is forced through the medium. Foam flow observations here, however, reveal that despite the network strength and connectivity, CFs can flow through and at higher flow rates retain their structures after being pumped through a porous environment. The rest of this chapter is thus devoted to explaining the intricacies behind how CFs flow through porous environments.

Three stages of foam flow were observed when CFs were pumped through the micromodel: I) an initial stage that consists of particle clusters in suspension flowing through the pores, II) a middle stage where bubbles and particle clusters co-flow or alternate through the micromodel, III) a final stage chiefly consisting of large bubbles

invading the micromodel pores. Figure 5-4 shows images of the micromodel during each stage of CF flow.



Figure 5-4 Different stages in capillary foam flow a) initial particle cluster flow, b) coflow of particles and bubbles and c) large bubble invasion of pores

The CFs pumped through the micromodel in this work have low gas volume fractions ( $\phi_g \sim 30\text{-}40 \text{ vol. \%}$ ) compared to typical surfactant foams ( $\phi_g > 80 \text{ vol. \%}$ ) and are inherently wet foams. When the foam is pumped from bottom to top as shown in Figure

5-2, the water and particle suspension at the bottom of the CF is first displaced and flows through the pores of the micromodel. CF flow in this stage (i.e., stage I) is observed to progress without any clogging. As the flow continues, the particle clusters entering the pores become denser and few pores begin to entrap some particle clusters, likely because of the affinity of the pore walls for the oil that bridges the particles. The flow of particle clusters in suspension occurs only for a few seconds relative to the entire foam flow experiment, as bubbles start to invade the pores shortly after the denser clusters flow through the micromodel. In stage II, co-flow of bubbles and particle clusters change the flow dynamics within the pores as more pores entrap both bubbles and particles and thus reduce the number of flowing paths available to the foam within the micromodel. In stage II, bubbles and particle clusters move through 1-2 available paths in the micromodel. Although the foam flow pathways occasionally change during this stage because existing paths clog and others are freed up, the overall sweep of the micromodel volume is high with few dead zones observed. Towards the end of the foam flow, as the top region of the CF in the syringe propagates through the micromodel, larger bubbles, and fewer particle clusters flow through the pores in stage III. CF flow in stage III, compared to stages I and II, is not as continuous because more clogging events occur, which potentially stem from the flow of drier and larger bubbles at the top of the foam head.

Figure 5-5a shows the pressure differential  $(\Delta P)$  versus dimensionless time  $(\hat{t} = t/t_f)$  measured across the micromodel at different stages when CFs are pumped at varying flow rates. At all flow rates explored, the pressure drop across the micromodel increases as the CF is pumped from bottom to the top (of the syringe). The points in plot at which  $\Delta P = 0$ , correspond to gaps in the pressure reading with time. The pressure
differential for the highest and middle flow rates steadily increases during the experiment and eventually exceeds the capacity of the pressure sensor (220 kPa) when the top segment of the CFs is pumped towards the end of the experiment. In contrast, the pressure increase at the lowest flow rate is not as pronounced as that of the higher flow rates;  $\Delta P$  remains below 70 kPa for the duration of the experiment when  $\dot{v} = 0.1$  ml/min.



Figure 5-5 Pressure differential versus dimensionless time  $(\hat{t} = t/t_f)$  required to mobilize capillary foams through the micromodel at different pumping speeds. b) apparent viscosity of capillary foam

The different stages of CF flow discussed above correspond to segments of the pressure differential measurements shown in Figure 5-5a. In stage I ( $\hat{t} \leq 0.2$ ), the particle clusters flow easily through the micromodel and  $\Delta P \leq 10$  kPa. This occurs because the clusters are well solvated and do not hinder foam flow by clogging the pores. However, a pressure increase is observed within moments of entry of the first set of bubbles and dense particle clusters in stage II ( $0.2 \leq \hat{t} \leq 0.65$ ). The increase in  $\Delta P$  at  $\hat{t} \sim 0.2$  results from the initial entrapment of bubbles and particle clusters within pores that limit the available

pathway for foam flow. The pressure increase continues as CFs are mobilized through available the paths while leaving dead zones (portions without flow) in the micromodel. When foam flow in stage II is constant through a path(s),  $\Delta P$  is nearly constant, but this typically only lasts for few tens of seconds at most. In stage III ( $\hat{t} \ge 0.65$ ), sharp increases in  $\Delta P$  are observed as CF flow becomes difficult due to clogs, compressibility, and mobilization of large bubbles. The high  $\Delta P$  in this regime results in foam mobilization through the pores; the pressure significantly decreases when foam flow occurs but increases again when foam flow is slowed or halted by clogs.

The pressure drop in the foam flow experiment measures the flow resistance within the system, of which the foam viscosity and clogging are major contributors. The measured  $\Delta P$  required to mobilize the CFs can thus be related to viscosity ( $\eta$ ) through the Darcy law

$$\dot{v} = \frac{kA}{\eta L} \Delta P , \qquad (5-1)$$

where k is the absolute permeability of the medium, A is the cross-sectional area and L is the length of the flow path. Considering only the flow segments where  $\Delta P$  is relatively stable, the apparent viscosity of CFs at the imposed flow rates is estimated in Figure 5-5b with the following assumptions in mind: 1) the CF flow through the micromodel is homogenous, 2) the absolute permeability can be approximated via the scaling argument of the Kozeny-Carman equation. The viscosity plot in Figure 5-5b shows that the viscosity of CFs flowing through the micromodel increases with  $\Delta P$  and decreases with flow rate. While the linearity of the data points in Figure 5-5b is trivial because of the pressureviscosity relationship in Darcy's law, the magnitude of the CF viscosities shown is not. The apparent viscosity obtained at the intermediate and high flow rates are higher than the viscosity of water and comparable to various crude oil viscosities by an order of magnitude.<sup>21-23</sup> The decrease in foam viscosity with shear rate is also in line with the shear thinning behavior observed from rheology measurements on CFs in Chapters 2 and 4. The inset plot in Figure 5-5b highlights the CF viscosity at  $\dot{v} = 0.1$  ml/min and shows that the viscosity at the lowest flow rate, is orders of magnitude lower than the viscosity at the high and intermediate flow rates. The low viscosity here indicates a low flow resistance that likely occurs due to a high degree of CF breakdown, resulting from phase separation at the lowest flow rate; the CF viscosity and  $\Delta P$  correlates with an increasing in the gas volume fraction ("foam quality")  $\phi_g$  in CFs; note that higher viscosities are obtained at higher pressures, when more bubbles (in number and size) are present in the CF. The increase in foam viscosity with foam quality is well known in classical foams and high-quality foams are often used as displacing fluids for oil recovery because more bubbles can restrict gas mobility and divert fluid flow from high to low porosity regimes.<sup>4, 16, 24</sup>

The overall increase and fluctuations in  $\Delta P$  point to a lack of consistency in the flow of CFs through the micromodel and indicate that CF flow does not approach "steady-state" during the foam flow experiments. One potential reason for the fluctuations in  $\Delta P$  during CF flow could be the multiphasic nature of CFs. The flow of different phases (water, particle clusters and bubbles) through the porous medium could lead to fluctuations in  $\Delta P$ . Although the particle network and bubbles in CFs are connected by oil bridges, it is plausible that some connections are broken down to suspension of bubbles and particle clusters in water during flow. At low flow rates, phase separation of the foam into plugs of water, gas, and suspension, can be observed in the piping before the foam approaches the

micromodel. The fluctuations in  $\Delta P$  can also result from the level of clogging of the pores in the micromodel. We will explore, in the next section, how varying degrees of clogging with time, change the driving force required to mobilize the CFs through the micromodel.

## 5.3.2 Bubble and Particle Dynamics

Particles and bubbles trapped within the micromodel contribute to the overall flow resistance and lead to spikes in  $\Delta P$ . Particles and bubbles can clog the micromodel partially or completely. Partial clogging occurs when foam flows through only few channels because bubbles and particles are trapped in some of the pores while complete (or full) clogging occurs when foam flow is hindered across the entire micromodel for at least 5 seconds. Regardless of the imposed flow rate, we observed that the micromodel is partially clogged for most of the CF flow duration. On the other hand, the occurrence of complete clogging varies with flow rate and its duration is unpredictable. Figure 5-6a shows the number of complete clogging events observed at different flow rates when  $\sim$ 7 ml of CF is pumped through the micromodel. The plot shows that the occurrence of complete clogs in the micromodel decreases with increasing flow rate and suggests that a higher foam flow rate may preclude clogging of CF in porous environments. The number of complete clogs correlates with the spikes and fluctuations in  $\Delta P$  seen at different flow rates in Figure 5-5a; more fluctuations in  $\Delta P$  are observed at the lowest flow rate than at the intermediate and high flow rates.



Figure 5-6 a) number of full clogging events with flow rates, b) pressure required to mobilize CFs and percent of micromodel clogged at different pressures

Clogs occurs when the driving pressure is unable to overcome the resistance of capillary forces from bubbles and oil bridges in particle clusters. Foam flow in a porous environment is influenced by viscous and capillary forces and can be understood using the capillary number (Ca), the dimensionless number that balances both forces. In this case, the viscous force is a function of the applied pressure upstream from the pump while the capillary forces come from the interfacial tension in the flowing foam. When capillary forces significantly dominate viscous forces, as is the case when flow velocity is low, foam flow is more challenging, and can lead to clogging. The low and slow build of pressure at low flow rates suggests that the capillary forces resist the applied pressure and thus only a small portion of the CF is mobilized at a given interval when the foam yields to the applied pressure. At higher flow rates on the other hand, the higher driving force helps to mobilize CFs through the device with fewer clogs, because capillary forces are easily overcome. Furthermore, as pressure builds in system, the bubbles in CFs coarsen and contribute to the capillary pressure that further resists foam flow.

Clogging in CF flow can be resolved through pressurization, water erosion, and path switching. Pressurization at the inlet of the micromodel resolves clogging by forcing the CFs through the micromodel channels at high pressure; the inlet pressure drops significantly when foam flow continues, and the clog has been cleared. In water erosion, a current of water sweeps away particles and bubbles trapped in the pores of the micromodel and opens new channels for foam flow. Water erosion can occur through a process reminiscent of viscous fingering, where water flows through the porous CF matrix, as described in Chapter 4. Path switching on the other hand, occurs when a new flow path(s) opens as the existing path(s) closes. Because the foam flow takes the path of least resistance and some pores are less clogged than others, path switches take place when the clogging of another path in the micromodel is weak. We observed that one or more of these clog alleviation processes can take place simultaneously; for example, path switching can occur during water erosion. Partial mobilization, when CFs flow through one or two channels after a complete clog, can occur via all the above-mentioned processes; we note however that water erosion and pressurization typically alleviate clogs in multiple channels and lead to "full mobilization".

The fraction of the micromodel clogged during CF flow correlates with the pressure drop. In Figure 5-6b, the fraction of the micromodel volume that is clogged by trapped bubbles and particles is plotted as a function of the measured pressure drop during phase II and III of the CF flow. The clogged percentage of the micromodel is obtained via image processing described in Section 5.2.7 above. The plot shows that at low pressures  $(\Delta P \leq 35 \text{ kPa})$ , except for the blue circle at  $(\Delta P = 17 \text{ kPa})$ , at least 70% of the pore volume is clogged. When pressure builds to mid pressure ranges,  $35 \leq \Delta P \leq 120 \text{ kPa}$ , roughly half of the micromodel is clogged after partial mobilization and when  $\Delta P > 120$  kPa, 35% or less of the pore volume is clogged. The low pressures and high clogged volume points (black squares) in Figure 5-6b denote foam flow through 1 or 2 channels in the micromodel and represent the major pattern of CF flow through the micromodel without clogging. The higher-pressure data points at  $\Delta P > 120$  kPa (blue circles), with lower clogged volumes, capture the pressure required to alleviate clogging and induce mobilization of CFs through multiple channels in the micromodel.

When CF bubbles are not clogging the micromodel, they flow through pores, interact with one another and with the micromodel constrictions and exhibit different mechanism of generation, propagation, and destruction in the process. Figure 5-7a-c, show lamella division, pinch off and snap off bubble division and generation mechanisms observed in CFs. Lamella division in CFs, shown in Figure 5-7a, occurs when a mobile bubble encounters a constriction that causes the flow to branch in two directions. The bubble stretches around the constriction, flows in both directions, and divides into two separate bubbles that continue translating downstream.<sup>25-26</sup> Figure 5-7b highlights the recently discovered pinch off mechanism that involves the interaction of two or more bubbles flowing through a constriction.<sup>27</sup> During pinch off, the bubble passing through a constriction is broken into separate pieces by a neighboring bubble attempting to pass through the same constriction. The more common snap off mechanism was also observed in CF flow and is shown in Figure 5-7c. As described by Radke and Kovscek, snap off is a mechanical process that repeatedly occurs in multiphase flow.<sup>4</sup> Snap off occurs when a bubble enters a pore constriction and the liquid around the pore neck causes instability and leads to the "snap-off" of a new bubble.<sup>28-29</sup> Snap off is the dominant mechanism observed when gas and surfactant solution are co-injected to form high quality surfactant foams in porous media.<sup>4, 30</sup> In contrast, we observed that lamella division is the dominant bubble division mechanism in CFs flowing through the micromodel. Lastly, we note that the leave behind mechanism was not observed likely because the low gas volume fraction in CFs predominantly precludes continuous gas foams in the micromodel.



Figure 5-7 Showing bubble division and generation mechanisms of a) lamella division, b) pinch off, c) snap off and d) coalescence observed in capillary foams

Lamella division depends on the bubble size and occupancy of the surrounding pores. Bubble division is observed to generally occur when the size of the approaching bubble exceeds the pore constriction size. In a few cases, however, bubbles smaller than the constriction can also divide rather than flowing through one of the pore constrictions unaltered. Lamella division can also be prevented when bubbles or particles are trapped in neighboring pores. Stationary bubbles or particle clusters in adjacent pores prevent the bubble from dividing and force the approaching bubble to squeeze through the pore in one direction. Lamella division occurs multiple times throughout CF flow in the micromodel. Medium size bubbles can divide as much as 2-3 times before reaching the pore size and the number of divisions are observed to increase with bubble size.

Although none of the above-mentioned bubble mechanisms are unique to CFs and have previously been observed and studied in surfactant foams, it is quite surprising that these mechanisms are observed in CFs because CFs do not contain surfactants that can quickly stabilize the interface of newly created bubbles. When new bubbles are created, the presence and size of surfactants enables relatively fast stabilization of the newly generated air-water interface and prevents coalescence of the new bubble with other bubbles. In capillary foams however, the particles that help stabilize the interface are orders of magnitude larger than surfactants and cannot diffuse speedily to cover the new interface. We suspect that the oil-coats around the CFs bubbles reduce phase separation kinetics while particles populate the newly created interface and lower the interfacial tension.

In addition to the highlighted bubble division and generation mechanisms, CF bubbles flowing through the micromodel combine with one another in coalescence events and large bubbles often flow through multiple pores unperturbed. As shown in Figure 5-7d, coalescence of gas bubbles occurs when one bubble encounters another bubble flowing in the same path. Coalescence in foams typically involves rupturing of thin films separating two bubbles. Given that CF bubbles are stabilized by an oil-particle composite that ought to create thick films, coalescence is favored and likely to occur in bubbles with interfaces

that are not adequately coated by oil or surrounded by particles. Large bubbles, that are created by coalescence or enter the micromodel as gas plugs, often span multiple pores and can usually translate through the micromodel without undergoing any division (see Figure 5-4c). These gas plugs tend to invade multiple pores but only advance through one major path; on exiting the micromodel, the branched gas fronts recede from the adjacent pores and flow through the path.

The different mechanisms of generation, division, and destruction lead to changes in sizes and numbers of bubbles flowing through the micromodel. The number of bubbles generally increase while the sizes of bubbles are observed to decrease with increasing distance from the entry point of the micromodel. Figure 5-8a shows the plot of the average bubble sizes (in diameters of a sphere) measured as a function of position within the micromodel. The plot shows that the bubbles entering the micromodel are polydisperse and have an average size that is  $\sim 1.4x$  larger than the constriction spacing in the micromodel (100  $\mu$ m). As the bubbles move through the first set of constrictions and pores, the average bubble size decreases along with the variation in bubble size. No significant changes to the bubble sizes and variations are observed in the middle of the micromodel at positions  $0.4 \le x/L \le 0.7$  and the bubble sizes further decrease towards the exit/end of the micromodel. The average size of bubbles exiting the micromodel (90  $\mu m$ ) is slightly lower than and comparable to the constriction length. The bubble sizes in Figure 5-8a do not linearly decrease and plateau towards the micromodel exit as would be expected if bubble division alone occurs. We conjecture that the consistency in the average bubble sizes and variations, observed at the middle positions of the micromodel, results from a balance of bubble generation and destruction events where bubble sizes decrease because of bubble

generation events and bubble sizes increase because of coalescence. The net bubble generation estimates the balance in the rates of bubble generation and bubble destruction and can be obtained as a ratio by comparing the number of bubbles leaving to the number of bubbles entering the micromodel as shown in Figure 5-8b.





Figure 5-8b highlights the spread of the number of bubbles exiting the micromodel compared to the number of bubbles entering during a period of 0.25 s for three different samples. The inset plot shows the net bubble generation ( $R_{0/1}$ : ratio of the number of bubbles exiting versus entering the micromodel) for all the samples explored; the ratio of

colored samples corresponds to the samples in the main plot. The main plot in Figure 5-8b shows that most of the scatter points are above the x = y line, indicating net positive bubble generation, *i.e.*, there are more generation than destruction events in general. The ratio in the inset plot measures the degree to which division and generation events dominate destruction events and further shows that, in some cases, the generation events can exceed destruction events by up to 7 times. We observed that the samples with higher net bubble generation ( $R_{O/I} \ge 3$ ) correlate to flow of CF bubbles during a full or partial mobilization of the micromodel due to pressurization and that samples with  $R_{O/I} \approx 1$  or slightly higher correlate to steady flow of CFs at relatively constant  $\Delta P$ . The main plot in Figure 5-8b shows that the ratio of bubbles entering and exiting the micromodel, for a defined period, can vary significantly depending on the flow behavior observed. For steady flow (blue circles and green triangles), the scatter can be small or large with the bubble numbers varying based on the  $R_{O/I}$  magnitude within the period. However, for a full or partial mobilization (red diamonds), the scatter is very large with a higher bubble sample and  $R_{O/I}$ .

The observations recorded here suggest that bubble dynamics in CFs flowing through a porous environment depend on the foam mobility which is influenced by clogging. The observed pore clogging, by bubbles and particles in CFs, could potentially enable fluid diversion that improves oil displacement from underground reservoirs. This hypothesis is tested in the next section on crude oil displacement from the micromodel.

## 5.3.3 Crude Oil Displacement Study

The efficacy of CFs for EOR operations was probed in oil displacement experiments involving CF and water flooding of micromodels soaked in crude oil. The sweep efficiency in CF and water flooding were compared to determine the benefit of using CFs over water in crude oil recovery. Figure 5-9 shows a time series of images captured during crude oil displacement, by CF and water flooding, from the micromodel. The black portion of the images represent the crude oil phase while the white/grey parts correspond to portion displaced by CFs or water. We observe that both water and CFs are capable of displacing crude oil; however, the flooding images reveal that, at equivalent fluid volumes and flooding time, CFs sweep a greater percentage of the micromodel and displace more crude oil than water.





From Figure 5-9, we observe that the initial stages of CF and water flooding are quite similar, however CFs sweep more of the micromodel with time because the foam aids fluid diversion by blocking some of the pores it occupies. During the first 2 minutes of CF flooding, aqueous particle suspension flows through the middle portions of the micromodel

creating fingers or channels through the crude oil (see Figure 5-9a). As flooding progresses, bubbles and particle clusters flow through the micromodel following the pathway created by water and are trapped in the pores. The trapped bubbles and particles create enough capillary pressure to divert CF flow to portions of the micromodel still containing oil because flow occurs in the path of least resistance. The new paths formed through foam diversion gradually connect to existing paths and foam diversion continues till the CFs reach the edges of the micromodel. CFs are observed to displace crude oil by pushing the oil through paths previously emptied of oil. After 15 mins of CF flow, most of the pores are filled with CFs, however there is still residual oil around the pore constrictions and at the top and bottom right edges of the micromodel (see Figure 5-9a). We note that most of the black pixels in the middle sections of the images are particle clusters that are trapped in the micromodel pores, not oil.

In water flooding, most of the water flows through oil emptied pores in the micromodel. Water displaces crude oil from certain pores but leaves oil behind in some pore constrictions (see Figure 5-9b). The channels of water created through the crude oil are mostly continuous however that drops of water-in-oil can be observed in some cases. Although the water channels branch out toward the micromodel edges, fluid diversion in water flooding is not as strong as in CF flooding. In both cases however, oil displacement begins in the middle and moves outward towards the edges.

The measured pressure drop across the micromodel during the displacement experiments suggests that oil displacement is continuous during CF flooding. The plots in Figure 5-10 show the pressure drop measured over the course of the CF and water flooding experiments. During CF flooding,  $\Delta P$  continuously increases with time whereas in water

flooding,  $\Delta P$  increases initially, peaks at  $t_d \approx 0.12$ , and gradually decreases below the pressure detection limit (7 kPa) at  $t_d \approx 0.4$ .



Figure 5-10 Pressure differential measured over time during flooding experiments to displace crude oil from micromodel.

The observed trends in  $\Delta P$  corroborate the displacement patterns described above.  $\Delta P$  steadily increases in CF flooding as bubbles and particles clog pores emptied of oil and divert foam flow to oil containing pores, thus leading to higher pressures. The fluctuations in  $\Delta P$  likely correspond to periods of oil displacement or new path formation that allow for foam flow through the pores. In water flooding on the other hand,  $\Delta P$  increases as water initially penetrates the micromodel and creates paths through the oil. The pressure decreases thereafter because most of the water flows through the micromodel via continuous water pathways formed and is not diverted to the remaining oil containing pores in the micromodel.

Comparisons between oil displacement observations from CF flooding, in this work, and surfactant foam (SF) flooding in previous studies on EOR, indicate that more CFs will be required to displace oil from porous media.<sup>7</sup> The results on oil displacement by SFs, in different types of micromodels, show that a majority of the oil can be removed after injection of foam volumes on the order of tens of pore volumes (PV). Osei-Bonsu, et al. showed displacement of 80-100% of Isopar V oil from a 3D printed homogenous micromodel after injecting 3-6 PV of high-quality SFs.<sup>11</sup> In a different study by Xiao, et al., crude oil was completely displaced from a heterogenous PDMS micromodel after ~4 PV of SFs were injected.<sup>10</sup> The highest PV of SFs required for oil displacement, from studies in the SF literature reviewed, is 20 PV.8 Although the CF volume required for oil displacement in this study was not quantified in PV, the CF volume injected, to achieve significant oil displacement from the micromodel, was 3 orders of magnitude larger than the micromodel PV and is not comparable to the SF volume used in previous studies. Given that the oil displacement studies highlighted above have different experimental set-ups and parameters, it is worth noting that both SFs and CFs displace more oil than water at equal injected volumes.

While the present first observations of oil displacement by CFs are unimpressive when compared to related studies with SFs, CF flooding for EOR cannot be dismissed altogether as the effects of parameters, such as gas volume fraction and fluid flow rates, on oil displacement in CF flooding remain unexplored. Moreover, studies of capillary suspensions containing small amphiphiles for in-situ modification of particles suggest the possibility of stable CFs, containing surfactants in addition to oil and particles, may be advantageous for EOR.<sup>31</sup>

## 5.4 Conclusion

The flow behavior of capillary foams (CFs) at the pore length scale was investigated using a PDMS templated micromodel. The dynamics of bubbles and particle clusters pumped through the micromodel at different speeds were observed via light microscopy and the required pressure drop to mobilize the foams across the micromodel was monitored. The efficacy of CFs in displacing crude oil from underground reservoirs was also probed in oil displacement experiments.

The results of this work show that CFs flow through porous environments but face significant resistances due to clogging of pores by particles and bubbles. The data shows that CF flow is not homogenous and three different regimes were identified during CF flow through the micromodel: particle flow, bubble and particle co-flow, and flow of large bubbles. The measured pressure drop required to mobilize the CF in these regimes was found to increase with the gas volume fraction and depend on clogging within the micromodel. Microscopy results reveal that more bubbles are generated than destroyed during CF flow through the micromodel. We observed that lamella division is the main mechanism of bubble generation throughout the explored range of flow rates and highlight other mechanisms of pinch off and coalescence observed in this study. When CF were applied in crude oil displacement experiments, micrographs showed that the studied CFs achieved a better sweep of the micromodel than water alone but failed to approach the reported sweep performance of surfactant-based foams. The work done in this study serves as a starting point to understand CF flow in porous media. More work will be necessary to conclusively evaluate the applicability of CFs for conformance control in enhanced oil recovery.

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# CHAPTER 6. CONCLUSIONS AND FUTURE WORK

### 6.1 Conclusion

Capillary foams (CFs) with their oil-coated bubbles and oil-bridged particle network, present a different mechanism of foam stabilization and a foam architecture that influences foam rheology and dynamics. Inspired by the need for stable, oil-tolerant and tunable foams in products and processes across the cosmetics, pharmaceutical, material processing, and energy industries,<sup>1-4</sup> this thesis aimed to determine the impact of the CF structure on foam rheology and understand how to tailor CF properties for use in various industries. The oil-tolerance of CFs especially makes these foams very attractive for oilfield applications in enhanced oil recovery (EOR) operations; for this reason, the feasibility of pumping CFs to displace crude oil from underground reservoirs was also explored.

The fundamental rheological properties of capillary foams were introduced through steady shear and oscillatory experiments done in this thesis. It was found that despite their low gas volume fractions, CFs are rheologically similar to surfactant foams with high gas volume fractions. Oscillatory measurements on CFs revealed a relatively high foam stability with steady moduli values spanning 48 h and a yielding behavior that is consistent with observations from steady shear measurements. The multiple rheological tests conducted characterized CF rheology as that of an aging solid with a yield stress.<sup>5</sup>

The presence of a yield stress and elasticity in CFs is quite remarkable, given the low gas volume fraction of the foam. However, to allow tailoring of CFs for different applications, the relation between these mechanical properties and the observed foam structure and constituent ratios was investigated. Combining observations from microscopy and rheology studies, this thesis showed that 1) the particle wettability not only determines the type of gel network formed, but also influences the prevalence of oil droplets included within the foam; 2) the stability and rheology of CFs are mainly a function of the particle volume fraction whereas the foamability and observed microstructure are sensitive also to the oil-to-particle ratio. The rheological properties observed in CFs indicate that low-quality foams can now be used in place of high-quality foams while maintaining similar benefits. Furthermore, the findings here significantly impact foam engineering by providing new routes to modify foam properties via oil-particle composites that induce capillary forces. While previously foam rheology could only be modified by its gas fraction, three additional parameters can now be employed to alter foams in products and process.

In the second half of this thesis, practical studies were conducted to provide clarity on the dynamics of CFs under pressure driven flow in different environments. The effects of stress on CFs pumped through a tube was studied and although the results here showed that CFs are considerably stable at most shear rates, it was discovered that the long-term effects of stress that weaken bridges and coarsen bubbles in CFs are linked to the aging phenomenon. Furthermore, the effects of stress on CFs at low shear rates, as seen in phase separation events, were shown to be mitigated by strong a gel-network that can be achieved at high particle concentrations. Controlling gel-strength to moderate foam aging, underscores an application of fundamental CF rheology knowledge and highlights a practical benefit of CFs over surfactant foams. Although particles can also be used to reduce foam aging effects in traditional Pickering foams, CFs require fewer particles to increase the gel-strength because the oil-particle network significantly enhances rigidity.

The final part of this work focused on applying CFs for EOR by first studying the bubble-particle dynamics of CFs in a porous micromodel and then evaluating the displacement of crude oil from the micromodel by CF flooding. It was observed that CF flow at the pore scale is significantly influenced by clogging of pores by particle clusters and bubbles; the level of clogging is dependent on the applied flow rate (or pressure) and can also affect the stability of the foam, as likewise seen in tubes. Furthermore, clogging, though disadvantageous to foam flow through pores, was observed to promote fluid diversion to oil filled pores during displacement experiments and thus increase the sweep efficiency and oil yield of foam flooding over that of water flooding. Micromodel displacement studies are the state of the art for testing the feasibility of foams for transport applications in porous media; they provide accurate indications of pore scale phenomena and for this reason, the findings on CFs from this work provide relevant evidence that the performance of CFs needs to be improved before application to EOR. A major suggestion from the observations of this study that could improve the performance of CFs in EOR, is to increase the foam quality and control the water content in CFs to maximize the fluid diversion capacity and thus further increase the oil displacement efficiency of CFs; part of the next section of this chapter is devoted to addressing this issue.

Overall, the discoveries in this thesis will be instrumental in creating commercial capillary foam products and engineering CFs for use in industrial processes such as enhanced oil recovery

### 6.2 Limitations and Future Work

Although this thesis has expanded the knowledge on CFs by providing rheological data for practical applications, there are certain limitations in this work that should be pointed out, some of which include that: 1) the rheology data presented here is geometry dependent and the measure of the mechanical properties observed may vary based on the desired application; 2) the CF rheology data is limited to short time windows relative to industrial application times; 3) the viscosity information on CFs flowing through tubes is lacking; 4) the data provided is lab scale and may not necessarily scale to industrial levels as expected. Addressing most of these issues is process inherent and time dependent, *i.e.*, the resources and time to address these issues are unavailable; these issues shall thus be left as gaps to be filled in the CF literature. In addition, some possible areas of exploration that are beneficial to moving this topic forward are introduced in the following sub-sections on future work.

#### 6.2.1 Continuous Production of Capillary Foams

Foam flow experiments conducted in chapters 4 and 5 involved a batch process of pumping different CFs that were prepared in syringes. For more practical purposes and uses in industrial settings, a continuous approach to preparing CFs is desired. Although foams can be generated via a myriad of techniques: mechanical, chemical, phase-transition, etc,<sup>6</sup> prior observations suggest that a high energy input mechanical process will be the most appropriate means for continuously generating CFs. Such a process will require intense mixing of the constituent elements that make up the foam (gas, water, particles, and oil) for at least 1-2 minutes. A proposed approach to achieving continuous CF production is through an inline mixer that can be fitted with multiple inlets, for all input materials, and a single outlet for the foam effluent.<sup>7</sup> In this case, CFs can be formed in the piping by mixing the oil-particle suspension with a gas stream or with blowing agents that can generate gas in-situ (e.g., baking soda plus heat). Another approach will be to use flow focusing microfluidic techniques that can create fluid dispersions.<sup>8-9</sup> While both processes will require high control of the inlet flow rates for mixing to occur in the right ratios, the flow focusing approach is more complex in design and operation because of the multiple fluid interfaces in CFs. However, the benefit of the flow focusing approach is that it produces more uniform bubbles than bubbles obtained from an inline mixer.

### 6.2.2 Modifying Gas and Liquid Content in Capillary Foams

One suggestion for improving the efficacy of CFs for EOR is to reduce the water content and increase the fraction of gas in CFs that are pumped into underground reservoirs. Incorporating this suggestion will involve controlling the gas volume fraction in CFs and draining the CFs of water after preparation.

While it is uncertain how well the gas volume fraction in CFs can be controlled, adding a gas stream at high pressure during CF production, could increase the gas volume fraction of CFs prepared through the inline mixing process. Once the CF is produced, however, the second step of draining the foam can be done via gravity separation in a floatation column. The major challenge after draining CFs is transporting the drained, and likely viscous, foam head from the top of the column to where it is needed.

#### 6.2.3 Fluid Displacement in Heterogeneous Medium

The crude oil displacement studies carried out chapter 5 of this thesis can be extended by evaluating the CF displacement of crude oil and other underground fluids (e.g., brine) from heterogenous micromodels. Although the micromodel used in the current study is homogeneous, the porous environment in underground wells consist of pores of different sizes, lengths, and shapes and are better represented by a heterogenous model. Heterogenous micromodels can be fabricated via soft lithography (PDMS templated devices), 3D printing, or by using a sandpack with different sizes of sand grains. Fluid displacement in a heterogenous medium will better indicate the performance of CFs by providing more accurate results on CF mobility and fluid diversion in underground wells with different porosities.

# 6.2.4 Temperature and Salinity Stability Studies on Capillary Foams

For successful application of foams in EOR, foams should remain relatively stable at elevated temperature and saline conditions of oil reservoirs. Unfortunately, many surfactants are thermally and chemically unstable under reservoir conditions, which compromises the viscoelasticity of foams. Xue et al., after studying surfactant stability at elevated temperatures up to 120°C and at salinity conditions of 14.6% total dissolved salt, noted that very few surfactants are stable under such conditions.<sup>10</sup> Singh et al. also observed that the addition of silica nanoparticles to surfactant foams significantly improves the stability of foams at temperatures up to 75°C.<sup>11</sup>

The stability of CFs at temperatures that mimic reservoir conditions should also be studied to determine the suitability of CFs for application in EOR. A potential approach to this study could follow the method of measuring the relative height of the bulk foam over time at different temperatures.<sup>11</sup> The analysis on temperature effects on CFs should be combined with work done by Wang on the ionic strength effects on foamability of CFs to understand how higher temperatures and salt concentration affects CF stability.<sup>12</sup>

### 6.3 Reference

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# **APPENDIX A. ADDITIONAL FIGURES**

# A.1 Additional Data on PVC Capillary Foams

A.1.1 Normal Force during Strain Sweep Oscillatory Test



Figure A-1 Plot of normal force of the foam during the increasing strain amplitude test.

A.1.2 Foam Quality in PVC Capillary Foams



Figure A-2 Volume fraction of air present in capillary foam at varying oil concentrations

### A.1.3 Controlled Stress Experiments in Couette Geometry

Controlled stress experiments were performed in a couette geometry without sandpaper affixed to the walls of bob or the cup. Figure A-3 shows the flow curve obtained from the controlled stress experiment in the couette geometry. The plot shows an initial increase in the stress with strain rate, followed by a slight stress plateau over a range of strain rates; this data trend is similar to the trend observed when the same experiment was carried out in the parallel plate geometry. However, we are unable to gather further data at higher stresses and strain rates because slip of the capillary foam at the walls of the instrument, prevents proper shearing of the foam during the experiment.





# A.1.4 Yield Stress of PVC Capillary Suspensions

Capillary suspensions were prepared by mixing PVC particles (10 wt. %), TMPTMA (2 wt. %) and DI water (88 wt. %) with a homogenizer. The stress-strain rate plot for the capillary suspension was obtained from a controlled stress experiment on a parallel plate rheometer. The red line in the plot denotes the inferred yield stress of the capillary suspension.



Figure A-4 Plot of stress versus strain rate for PVC capillary suspensions.

# A.2 Confocal Micrographs on Silica Capillary Foams

# A.2.1 Images of Capillary Foams from P<sub>1</sub> and P<sub>2</sub> Particles

Capillary foams (CFs) made from  $P_1$  were imaged via confocal microscopy at a very low oil-particle volume ratio  $\rho = 0.05$ . Figure A-5 below shows two different images of the CFs in the XY-plane. The bright spots in the Figure A-5 show that there are hints of oil droplets even at this low oil-particle ratio. This is not surprising given that  $P_1$  preferentially wets water and not the oil phase, as such the particles easily stabilize an oil-in water emulsion.



Figure A-5 Confocal micrographs of capillary foams at an oil-particle at an oil-particle ratio  $\rho = 0.05$ , and a particle volume fraction  $\phi_p = 0.92$  % of P<sub>1</sub> particles

Confocal micrographs in Figure A-6 show that the thickness of the oil coats around the bubbles increase with  $\rho$  and thus confirm the hypothesis that bubbles in CFs sequester much of the added oil at high oil-particle ratios (see Figure A-6c & f)



Figure A-6 Confocal micrographs of capillary foams obtained at lower magnification for different oil-particle ratios a, d)  $\varrho = 0.2$ ; b, e)  $\varrho = 0.5$ ; c, f)  $\varrho = 1$ , all at a constant particle volume fraction  $\phi_p = 0.92$  % of P<sub>1</sub> particles (capillary state, top row) and P<sub>2</sub> particles (pendular state, bottom row).



Figure A-7 Confocal micrographs of capillary foams at different particle volume fraction a, d)  $\phi_p = 0.68$  vol. %; b, e)  $\phi_p = 0.92$  vol. %; c, f)  $\phi_p = 1.38$  vol. %, all at a constant oil-particle ratio  $\varrho = 0.2$  of P<sub>1</sub> particles (capillary state, top row) and P<sub>2</sub> particles (pendular state, bottom row).

# A.2.2 Images of Capillary Foams from P<sub>3</sub> Particles

Capillary foams made from P<sub>3</sub> were imaged via confocal microscopy at different oil-particle ratios while keeping the particle volume fraction constant at  $\phi_p = 0.92$  %. Figure A-8 below shows images of the CFs in the XY-plane at the different oil-particle ratios ( $\rho = 0.2, 0.5, \& 1$ ). All the images below have been altered by increasing the brightness and contrast so that the bubbles in the CF structure can be seen easily. The structure of CF made from P<sub>3</sub> shows that there are barely any oil droplets even as the oil concentration is increased; this is likely because the oil primarily partitions into the bubble
coats, and many bubbles are formed when the more hydrophobic P<sub>3</sub> particles are used to produce CFs.



Figure A-8 Confocal micrograph grid of capillary foams at different oil-particle ratios a)  $\varrho = 0.2$ , b)  $\varrho = 0.5$ , c)  $\varrho = 1$ , all at a constant particle volume fraction  $\phi_p = 0.92$  % of P<sub>3</sub> particles

## A.2.3 Image Comparison of Capillary Foams made with all Particles

At higher magnification of the confocal images, we observe that under identical foaming conditions and for the present particle volume fraction ( $\phi_p = 0.92$  %.) and oil-particle ratio ( $\varrho = 0.2$ ), the gas volume fraction and average bubble size of the foams increase with particle hydrophobicity. In addition, the presence oil droplets and the visibility of the particle network decrease with increasing particle hydrophobicity.



Figure A-9 Confocal micrograph grid of capillary foams formed from: a) Particle type #1 (P<sub>1</sub>); b) Particle type #2 (P<sub>2</sub>); and c) Particle type #3 (P<sub>3</sub>) at an oil-particle ratio  $\rho = 0.2$  and particle volume fraction  $\phi_p = 0.92$  %.

## A.3 Rheology Data on Silica Capillary Foams

# A.3.1 Proof of Data Reproducibility

Two CFs were freshly prepared from P<sub>1</sub> particles at a volume fraction  $\phi_p = 1.38$  % and an oil-particle ratio  $\varrho = 0.7$ . Both foams were subjected to identical frequency sweep and controlled stress tests and the storage modulus and flow curves from the tests are shown in Figure A-10. The storage modulus and flow curves from both foam samples in the plots overlap with one another showing that the capillary foam rheology data is reproducible. Furthermore, the plots here also indicate that the range of uncertainty within the data is on the order of the size of the markers throughout most of the explored frequency and shear rate range.



Figure A-10 a) Plot of storage modulus at different frequencies when  $\gamma = 0.001$  and b) plot of stress versus shear rates of capillary foams made from P<sub>1</sub> particles when  $\phi_p = 1.38\%$  and  $\varrho = 0.7$ . Black squares are original measurements and red circle are repeats; both measurements were performed on separate but freshly prepared capillary foams.

*A.3.2* Frequency Sweeps and Controlled Stress Experiments on Capillary Foams from P<sub>1</sub> and P<sub>2</sub> Particles

We probed the rheology of capillary foams prepared with P<sub>1</sub> particles in oscillatory and controlled stress experiments. Capillary foams were prepared at different oil-particle ratios while keeping the volume fraction of P<sub>1</sub> constant at  $\phi_p = 0.92$  vol. %. Figure A-11a shows the yield stress ( $\sigma_y$ ) and the plateau moduli ( $G_0$ ) values obtained from the raw frequency sweep plots and flow curves shown in Figure A-11b&c respectively. The plateau modulus is defined as the flat portion of the storage modulus (G') curve: the region where the value of the modulus does not change significantly with the frequency ( $\omega$ ); this can be seen between  $0.1 < \omega < 10 \ rad \ s^{-1}$  in Figure A-11b. The yield stress is defined as the value of the stress in which a plateau is observed in the flow curve, this can be seen between  $10^{-2} < \dot{\gamma} < 10^2 \ s^{-1}$  in Figure A-11c. Both Figure A-11b&c respectively show that the moduli value in the frequency sweeps plots and the flow curves of CFs at different oil-particle ratios collapse on each other and indicate that the values of  $G_0$  and  $\sigma_y$  at these oil-particle ratios are all very similar. On the other hand, the moduli and flow curve of a Pickering foam, produced without the oil, have lower in values than those of a capillary foam, see grey open hexagons in Figure A-11b&c.



Figure A-11 Plots of rheological changes to the plateau modulus ( $G_0$ : squares) and yield stress ( $\sigma_y$ : circles) in capillary foams when the oil-particle ratio is varied at  $\phi_p = 0.92$  vol. %; b) frequency sweep plots showing the storage modulus versus frequency of capillary foams (solid symbols) and the corresponding Pickering foam (gray hexagons); c) flow curves showing the yield stress of capillary foams and the corresponding Pickering foam (gray hexagons) when P<sub>1</sub> particles are used.

We probed the rheology of capillary foams prepared with P<sub>2</sub> particle in oscillatory and controlled stress experiments. Capillary foams were prepared at different oil-particle ratios while keeping the volume fraction of P<sub>2</sub> constant at  $\phi_p = 0.92$  vol. %. Figure A-12a shows a comparison of the values of the yield stress ( $\sigma_v$ ) and the plateau moduli ( $G_0$ ) obtained for CFs prepared from both P<sub>1</sub> and P<sub>2</sub> particles. Figure A-12b & c also show the raw frequency sweep plots and flow curves obtained for CFs prepared from P<sub>2</sub> respectively. The plateau modulus in CFs made from P<sub>2</sub> is defined as the average of the storage modulus values obtained between  $0.1 < \omega < 10 \ rad \ s^{-1}$  in Figure A-12b. The yield stress in Figure A-12c, is defined in the similar manner as explained in the flow curves of CFs made from P<sub>1</sub>.



Figure A-12 a) Plots of rheological changes to the plateau modulus ( $G_{\theta}$ : squares) and yield stress ( $\sigma_{v}$ : circles) in capillary foams made from P<sub>1</sub> (closed symbols, capillary

state) and P<sub>2</sub> (open symbols, pendular state) when the oil-particle ratio is varied at  $\phi_p = 0.92$  vol. %. b) Frequency sweep plots showing the storage modulus of capillary foams and the corresponding Pickering foam (gray hexagons) when P<sub>2</sub> particle is used. c) Flow curves showing the yield stress of capillary foams and the corresponding Pickering foam (gray hexagons) when P<sub>2</sub> particles are used.

## A.3.3 Amplitude Sweeps on Capillary Foams from P1 and P2 Particles

Amplitude sweep experiments under oscillatory tests were conducted on capillary foams prepared with P1 and P2 particles. Capillary foams were prepared at different oilparticle ratios while keeping the volume fraction of P1 and P2 constant at  $\phi_p = 0.92$  vol. %. Figure A-13a & b show the raw storage modulus plots obtained from the amplitude sweep experiments on CFs prepared from  $P_1$  and  $P_2$  respectively. The plots in Figure A-13 show that the trend in the storage modulus of the CFs is consistent at all oil-particle ratios and for both particle types within the range of the applied strains of  $10^{-4} < \gamma < 10$ . G' remains flat in the linear viscoelastic regime ( $\gamma < 0.1$  for P<sub>1</sub> in the capillary state and  $\gamma < 0.03$  for P<sub>2</sub> in the pendular state) and continuously decreases beyond a strain of 10% for  $P_1$  and 3% for  $P_2$ . For both particle types (and network types), the values of G' are similar when  $\varrho \leq 1$ , as seen by the overlapping plots, and slightly decreases at  $\rho = 1.8$  due to weaker bridging at higher oil content, as discussed in the chapter 3. Figure A-13c shows the comparison between the storage and loss modulus plus and reveals that crossover between G' and G'' at  $\gamma \cong 2$  for CFs made with P<sub>1</sub> particles at  $\phi_p = 0.92$  vol. % and  $\rho = 1$ 



Figure A-13 Amplitude sweeps plots showing the storage modulus of capillary foams at different oil-particle ratios when a) P<sub>1</sub> particles are used (capillary state) and b) P<sub>2</sub>

particles are used (pendular state). c) G', G" comparison in capillary foams from P<sub>1</sub> particles.

#### A.3.4 Shear Viscosity of CFs from P<sub>1</sub> Particles



Figure A-14 Master curve showing the different slope regimes in the shear viscosity plot of silica/TMPTMA CFs at different particle volumes.

#### A.4 Foamability and Foam Stability in Silica Capillary Foams

*A.4.1* Foam Volume and Foam Quality of Capillary Foams Prepared from P<sub>1</sub> and P<sub>2</sub> Particles

Capillary foams were prepared at different volume fractions of P<sub>1</sub> and P<sub>2</sub> particles while keeping  $\rho$  constant and at different oil-particle ratios while keeping  $\phi_p$  constant. The initial and final foam volumes of CFs when  $\phi_p$  and  $\rho$  are varied are presented in Figure A-15a & b respectively while their corresponding foam qualities are presented in Figure A-15c & d. The comparative data for CFs prepared with P<sub>2</sub> particles are presented in Figure A-16a-d in a similar manner.



Figure A-15 Plots of capillary foam volume as a function of a) particle volume fraction  $(\phi_p)$  and b) oil-particle ratio  $(\varrho)$ ; plots of capillary foam quality as a function of c) particle volume fraction and d) oil-particle ratio when CFs are prepared with P<sub>1</sub> particles (foams in the capillary state). Initial values are represented by open symbols and final values are represented by closed symbols.



Figure A-16 Plots of capillary foam volume as a function of a) particle volume fraction  $(\phi_p)$  and b) oil-particle ratio  $(\varrho)$ ; plots of capillary foam quality as a function of c) particle volume fraction and d) oil-particle ratio when CFs are prepared with P<sub>2</sub> particles (foams in the pendular state). Initial values are represented by open symbols and final values are represented by closed symbols.

### A.4.2 Drainage in Capillary Foams from P<sub>1</sub> and P<sub>2</sub> Particles

The loss of water from CFs was monitored by measuring the foam volume change over a 2 h experimental time window. CFs were prepared at multiple oil-particle ratios while keeping the particle volume fraction of P<sub>1</sub> and P<sub>2</sub> particles constant. Figure A-17 below shows the plot of the change in the relative foam volume over the experimental time for P<sub>2</sub> when  $\phi_p = 0.92$  % and for P<sub>1</sub> when  $\phi_p = 1.38$  %.



Figure A-17 Plot of capillary foams volume change in time for different oil-particle ratios when a) P<sub>2</sub> is used for foaming at  $\phi_p = 0.92$  % and b) P<sub>1</sub> is used for foaming at  $\phi_p = 1.38$  %

The plot in Figure A-17a shows that CF volume decrease with time is also independent of  $\varrho$  when P<sub>2</sub> particles are used to prepare CFs. Figure A-17b shows that, for a higher particle volume fraction of the condensed phase, the CF volume does not change much within the first 2 h after foam preparation. The relative foam volume change when  $\phi_p = 1.38$  % is low here because very little water is lost from the foam, a result of a stronger particle network. Both plots also show that  $\varrho$  does not affect foam stability in CFs and Figure A-17b confirms that drainage is reduced at higher particle volume fractions.



Figure A-18 Images of bulk capillary foams ( $\phi_p = 0.68$  vol. %;  $\varrho = 1.4$ ) showing foam evolution from a) when t = 0 h to b) when t = 6 h after preparation of the foam.



Figure A-19 Plot of frequency distributions of bubble sizes in a) static and b) pumped capillary foams



Figure A-20 Images of capillary foams dyed with green food dye flowing through a polyethylene tube showing phase separation between (a) water and gas, (b) foam and water before entering the micromodel