POLY(HIGH INTERNAL PHASE EMULSION) FOAMS AND FIBERS: STRUCTURE-PROPERTY RELATIONSHIPS

by

CODY BEZIK

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Department of Chemical Engineering

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SCHOOL OF GRADUATE STUDIES

We hereby approve the thesis of

CODY BEZIK

Candidate for the Master of Science degree

(signed) Prof. Donald Feke

(Chair of the committee)

Prof. Ica Manas-Zloczower

Prof. Stuart Rowan

Prof. Daniel Lacks

(date) 5/14/2015
*We hereby certify that written approval has been obtained for any proprietary material contained therein.
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Abstract

by

CODY BEZIK

Poly(high internal phase emulsions) are highly porous open-cell foams formed by emulsion templating. These foams have many applications, but the fundamental relationship of emulsion properties to the final foam properties is not well understood, nor is the relationship between the morphology of the foam to its own properties. In this thesis, these relationships are further elucidated. It is shown that changing electrolyte concentration leads to changes in foam modulus, which are shown to be correlated with the internal surface area. Furthermore, this relationship is shown to peak at an intermediate value and is dependent on emulsion curing conditions.

The feasibility of creating novel poly(HIPE) fibers is also explored and demonstrated. It is shown that the surface porosity of the fibers can be tuned by additions to the curing bath, and that interfacial polymerization in the curing bath can result in a shell being grown on the fiber surface.
Chapter 1: Introduction

1-1: Poly(High Internal Phase Emulsions)

High internal phase emulsions (HIPEs) are emulsions defined by an internal phase concentrated above 74% - that is, more than 74% of the volume of the emulsion is composed of droplets. This limit is the geometric limit of rigid, closest-packed, monodisperse spheres. The droplets of an emulsion prepared above this limit are understood to have assumed shapes intermediary between spheres and polyhedra\(^1\). HIPEs can be used as templates for highly porous structures, known as poly(high internal phase emulsions), or poly(HIPE)s. This is accomplished by polymerizing the continuous phase of a water-in-oil (w/o) HIPE. The resulting structure is a solid foam with the dispersed phase embedded in it; once dried, these droplets leave behind “voids” and an open, highly porous structure remains. Another distinguishing feature of poly(HIPE)s is that during this polymerization, connections between the voids form, known as “windows”. These windows form as the external phase surrounding the internal phase droplets thins, leading to rupturing\(^2\). The final poly(HIPE) is a highly interconnected porous foam structure. Figures 1-1 and 1-2 demonstrate the formation of a poly(HIPE) and typical poly(HIPE) morphology, respectively. There are numerous possible applications for poly(HIPE) systems, including shape memory foams, membranes, scaffolds for tissue engineering, catalyst supports, and chromatographic applications.
Figure 1-1: A schematic of a typical poly(HIPE) formation. Adapted from Silverstein et. al.³

Figure 1-2: SEM of a typical poly(HIPE). This is a poly(styrene-divinylbenzene) system.
Adapted from Sergienko et. al.⁴
1-2: Factors Affecting Poly(HIPE) Morphology

The average void diameter has been shown to be sensitive to the concentration of electrolyte in the dispersed phase of a HIPE\(^5\). In reviews of literature to date, it has typically been cited that an increase in electrolyte concentration leads to smaller void diameters\(^6\). A typical series of foam structures with increasing electrolyte content is shown in Figure 1-3. Relating the change of cell size to an observable property of the foam, such as its Young’s modulus, has long been of interest. There are conflicting theories for what effect void diameter should have on mechanical properties. Gibson and Ashby do not predict any such dependence\(^7\); Williams et. al. suggested that smaller void diameters would lead to higher stiffness\(^5\); Ceglia et. al. suggested that larger void diameters would lead to higher Young’s modulus\(^8\). These differing ideas in the literature reveal a need to better understand how morphology of the foam affects its mechanical properties, as well as an understanding of how HIPE properties translate to poly(HIPE) morphology.

Factors affecting the void diameter are many and include most of the things that influence the properties of the HIPE, as well as the curing conditions. Higher mixer rates or times lead to smaller HIPE droplets (observed experimentally). The choice of oil phase components can also have an effect. The temperature at which samples are cured does not have a strong effect on final void diameter, but has been observed to affect the overall conversion of the system and thus its mechanical properties. Because of these possible affects, all of these parameters are controlled for in this thesis.

While void diameter is considered as the primary influence on mechanical properties, it is also possible that the strut thickness is an influence. In this work it is
largely assumed not be an influence. It is a difficult property to measure (likely requiring the use of transmission electron microscopy, TEM). Gibson and Ashby\textsuperscript{7} showed that porosity is proportional to strut thickness; since the samples used in this work are of the same nominal porosity, this is assumed to be an insignificant influence.
Figure 1-1: A series of foams containing potassium sulfate and initiated with AIBN. The labels below each image indicate grams of salt per 100 mL of water. Adapted from Williams et. al.\textsuperscript{5}
Small-scale porous polymer fibers are of potential use in a wide variety of applications. They have been discussed as useful materials for adsorption, ultrafiltration, ion-exchange resins, and as carriers for catalysts and reagents\textsuperscript{9,10,11}. Such materials are often produced via a technique known as electrospinning\textsuperscript{12}. In this technique, an electric charge is applied to draw fibers from a liquid, producing small fibers often on the micro or nano scale. Typically, a polymer is dissolved in an organic solvent – for example, poly(methyl methacrylate) (PMMA) can be dissolved in a binary system of dichloromethane/dimethylformamide (DCM/DMF)\textsuperscript{12}. Fibers of PMMA could then be drawn from this solution by electrospinning. An example of such fibers produced through this technique is shown in Figure 1-4.

The utility of such fibers lies in their high surface area and fundamentally porous nature. However, producing porous fibers by electrospinning has a flaw in that it relies on organic solvents. Many organic solvents are fire hazards, present health concerns, and are unfriendly for the environment. An alternative route to producing porous fibers that did not rely on the use of organic solvents would be useful. The possibility of utilizing poly(HIPE) systems to produce porous fibers would allow systems of similar surface area and porosity as fibers produced from electrospinning, without introducing undesirable organic solvents to the production process. Additionally, there are opportunities to vary the morphology of the poly(HIPE) fiber from the inner core to the outer shell.
1-4: Objectives

In summary, the objective of this work is to study (i) the relationship between HIPE properties, specifically electrolyte content, on final poly(HIPE) properties and (ii) the potential for creating poly(HIPE) fibers and manipulating their morphology.

The structure of this thesis is as follows:

- Chapter 2: A description of the experimental methodologies used in this work is described.
- Chapter 3: The relationship between HIPE composition and poly(HIPE) morphology and properties is explored.
- Chapter 4: The potential for the production of poly(HIPE) fibers and the possibility for manipulating their morphology is described.
- Chapter 5: Summary, conclusions, and future work are described.
Figure 1-2: A series of images representing different electrospun fibers. The original authors produced both nonporous (e) and porous (f) fibers. Adapted from Bae et. al.\textsuperscript{12}
References


Chapter 2: Experimental Methodology

2-1: Preparation of HIPE

HIPE samples were consistently prepared utilizing the same experimental set up. As an example, the composition of a typical HIPE system will be described, along with the procedure to synthesize the HIPE. A typical HIPE system used was composed of 95% internal (aqueous) phase and 5% continuous (oil) phase (by weight).

The oil phase was composed of a 3.35:1 ratio of 2-ethylhexyl acrylate (EHA, Sigma Aldrich) and ethylene glycol dimethacrylate (EGDMA, Sigma Aldrich). The EHA monomer becomes the main chain polymer in the poly(HIPE) system, and the EGDMA monomer becomes a crosslinker, giving additional mechanical strength and thermal stability to the poly(HIPE) system.

These monomers are miscible in the proportions used and are combined with polyglycerol succinate (PGS, Procter & Gamble) surfactant such that the surfactant is 12% by weight of the oil phase.

Figure 2-1: The monomers utilized in the system. EGDMA acts to crosslink while EHA is the main chain polymer.
The aqueous phase was composed of 2% sodium chloride (NaCl, Fisher Scientific) and 0.33% sodium persulfate (NaPS, Sigma Aldrich). While the specific effects of the electrolyte will be explored later in this work, NaCl generally acts to stabilize the emulsion; NaPS acts to initiate the radical polymerization to cure the poly(HIPE).

To synthesize the poly(HIPE), typically 8 g of the oil phase was added to a 500 mL bottle, then 139.5 g of a 2.18% NaCl solution was added in 3 minutes, 6 seconds via a digital gear pump (Cole-Parmer). This salt solution was warmed to 40 ºC by being circulated in an immersion circulator (Lauda), which allows the HIPE to form more readily. 12.5 g of a 0.04% NaPS solution was then added dropwise. While the aqueous solutions are being added, the mixture is stirred at 300 RPM by an overhead mixer (IKA). After the aqueous solutions have been added, 1 minute of additional mixing was allowed. This procedure is a general one laid out by Procter & Gamble for consistency with their results. Generally speaking, variations in mixing time and temperature as well as the chemical composition of the system can alter the final properties.
Figure 2-2: Above, the water circulator system used to deliver the salt solution to the HIPE mixing vessel. Left, the overhead mixer and the HIPE mixing vessel.
2-2: Curing Poly(HIPE) Monoliths

A typical process for curing poly(HIPE) in monolith form was to transfer via spatula 10mL of HIPE to a beaker of the same volume. This beaker was immersed in a silicone oil bath, which had been heated to 85°C. The samples were left to cure for 50 minutes, then extracted and stored in room temperature water. The effect of sealing the beakers was part of the experimental investigation; if the beakers were sealed, they were covered first in Parafilm and then in aluminum foil. Figure 2-2 shows the sealed and unsealed beakers, and a curing in progress.

Figure 2-3: Below, unsealed and sealed 10mL beakers containing uncured HIPE. Left, a curing in progress; the beakers are immersed in heated silicone oil.
2-3: Making Poly(HIPE) Fibers

The approximate time to form a covalently bonded network in a HIPE has been demonstrated to be about 110 seconds at 85°C\(^1\). The injection of a HIPE jet from a syringe at a rate of approximately 0.12 mL/min into a heated water bath at this temperature allows the HIPE to cure before it would otherwise break up due to Rayleigh instability. To allow for complete curing, fibers are allowed to remain in the elevated temperature bath for 10 minutes. These fibers are extracted from the curing bath and stored in room temperature water. A typical experimental setup for the curing of poly(HIPE) fibers is shown in Figure 2-3.
2-4: Optical Microscopy

The HIPEs before curing were examined using an optical microscope (SOURCE). An optical microscope uses light and a system of lenses to provide high resolution images of small-scale samples. A lens close to the...
object of interest (a HIPE sample) focuses an image of the sample, which is magnified by a system of lenses to give an enlarged image of the sample. This simple and classical technique allows study of the size and size distribution of droplets in the HIPE.

2-5: Stress-Strain Testing

The stress-strain curve for poly(HIPE) monoliths was determined using an MTS Universal Testing System operated in compression mode. The machine operates by placing a sample of known diameter and height in between a fixed plate and a crosshead which lowers and compresses the sample at a determined rate (1 mm/min). A stress-strain curve is generated from which Young’s modulus of compression (E) is calculated, being the ratio of stress to strain in the Hooke’s law region of the curve; Young’s modulus provides a measure of stiffness of the material and is a convenient mechanical property to examine.

2-6: Scanning Electron Microscopy

A scanning electron microscope (SEM, SOURCE) was used to probe the internal structure of the poly(HIPE), which exists on the micron scale. SEM produces images of a sample by scanning it with a focused beam of electrons. The interactions of the electrons with the atoms in the sample produce signals which are detected by the SEM. These signals are translated into information about the surface of a sample and are reassembled into an image with resolution on the nanometer scale possible.
2-7: Surface Area Measurement

The surface area of a poly(HIPE) sample can be determined by physical adsorption of a gas (nitrogen) onto the surface of the sample and calculating the amount of adsorbed gas that corresponds to a monolayer on the surface. The Brunauer, Emmet, and Teller (BET) adsorption isotherm equation is used to translate the acquired data into specific surface area. The data were acquired with SOURCE. The BET adsorption isotherm equation is:

\[ \frac{1}{V_a \left( \frac{P}{P_0} - 1 \right)} = C \frac{1}{V_m C} \left( \frac{P}{P_0} \right) + \frac{1}{V_m C} \]  

(1)

In the above equation\(^2\), \(P\) is the partial vapor pressure of the adsorbate in equilibrium with the surface at the boiling point of liquid nitrogen; \(P_0\) is the saturated pressure of the adsorbate; \(V_a\) is the quantity of adsorbed gas; \(V_m\) is the volume of gas adsorbed at STP (0°C and 100 kPa) to produce an apparent monolayer on the sample surface; \(C\) is the “BET constant”:

\[ C = \exp \left( \frac{E_1 - E_L}{RT} \right) \]  

(2)

\(E_1\) is the heat of adsorption for the first layer and \(E_L\) is the heat of adsorption for subsequent layers. In an adsorption test, a value of \(V_a\) is measured, and the “BET value” (the left hand side of Equation 1) is plotted against \(\frac{P}{P_0}\). This yields a straight line, the slope and intercept of which provide values for \(V_m\) and \(C\). Specific surface area can be calculated with the following equations:

\[ S_{total} = \frac{V_m N_S}{V} \]  

(3)
\[ S_{BET} = \frac{S_{total}}{a} \quad (4) \]

In Equation 3, \( S_{total} \) is the total surface area of the sample, \( N \) is Avogadro’s number, \( s \) is the effective cross sectional area of an adsorbate molecule, \( V_m \) is the molar volume of the adsorbate gas, and \( a \) is the total mass of the sample.

**2-8: Thermogravimetric Analysis**

Thermogravimetric analysis (TGA) was carried with a Q500 (TA Instruments). A TGA experiment entails measuring the change in weight of a sample through changes in temperature or time. Samples in this work were tested according to a “heat and hold” method where temperature was ramped at 20°C/minute to a temperature of 65°C, at which point the testing conditions were held isothermally until the end of the experiment. The change in weight over time allowed extraction of information about the drying of poly(HIPE) fibers, as well as their total porosity.

**2-9: Ultraviolet-Visible Spectroscopy**

Ultraviolet-visible spectroscopy (UV-Vis) is an absorption spectroscopy technique taking place in the ultraviolet/visible region. The technique functions by exciting nonbonding electrons in a sample as they absorb light. The specific wavelength of light absorbed by a sample is characteristic of a material and the intensity of its absorbance is characteristic
of its concentration in solution. In these experiments a spectrophotometer was used. A spectrophotometer measures the intensity of light before and after passing through a sample; the ratio of the two is called *transmittance*, which is related to its *absorbance*. A typical output of a spectrophotometer compares absorbance to the wavelengths scanned in an experiment; peaks indicate strongly absorbing regions and can identify the materials, and comparing the relative intensity of peaks in solutions of the same material is a way to compare relative concentrations.
References


Chapter 3: Effect of Electrolyte Concentration on Poly(HIPE)

3-1: Emulsion Stability

The relationship between the morphology of an uncured, room temperature HIPE is not necessarily directly translated to the morphology of the final, cured poly(HIPE)\(^1\). The conditions a HIPE is subjected to while it cures can have dramatic effects on its morphology. In particular, the high temperature conditions and possible evaporation of water can affect droplet coalescence and Ostwald ripening (the two major processes governing stability in HIPE). These effects exist in balance, and it is proposed here that it can be disrupted by raising the temperature of the HIPE or allowing water to evaporate from the system.

Ostwald ripening (in a HIPE system) is essentially the diffusion of water from small droplets to large droplets\(^2\). Figure 3-1 provides a schematic illustration. In a two liquid system where the liquids have finite mutual solubility and the droplets are polydisperse, there will be a difference in chemical potential between large and small droplets. Small droplets are more soluble than larger ones, owing to the change in surface free energy due to curvature. Molecules from the surface of these smaller droplets diffuse into the continuous phase, and then diffuse into the larger droplets. Thus, in any HIPE, there is a preference for larger droplets and the likelihood that small droplets will become part of larger ones, increasing droplet diameter, decreasing interfacial area, and reducing the stability of the emulsion\(^3\). A
mathematical understanding of the rate of Ostwald ripening was produced by Lifshitz, Slezov, and Wagner\textsuperscript{4,5}, leading to LSW theory and the equation:

$$\omega = \frac{dr^3}{dt} = \frac{8DC_{\infty}V_m^2\gamma}{9RT} \quad (1)$$

where $\omega$ is the ripening rate, $r$ is the radius of the particles, $D$ is the diffusion coefficient of the dispersed phase in the continuous phase, $C_{\infty}$ is the solubility of the dispersed phase at the interface, $V_m$ is the molar volume of the dispersed phase, $\gamma$ is the interfacial tension between phases, $R$ is the gas constant, and $T$ is the absolute temperature. LSW theory was derived for a solid matrix, but it has since been demonstrated to apply for w/o emulsions\textsuperscript{3}. It has been demonstrated that introducing into the dispersed phase a component that is soluble in it but not in the continuous phase (\textit{e.g.} an electrolyte) can inhibit Ostwald ripening, by inhibiting the diffusion of molecules outward\textsuperscript{6}; it does so by producing an osmotic force that counteracts the driving force for Ostwald ripening.
The mechanism of coalescence is fundamentally different from that of Ostwald ripening. In HIPE, droplets coalesce by film rupture, i.e. when droplets press against one another, the oil phase separating those droplets bursts and the droplets merge together into one, larger droplet. Figures 3-2 provides a schematic illustration.

Figure 3-1: A schematic representation of Ostwald ripening, as molecules from small droplets diffuse outward and into larger droplets\textsuperscript{7}.

Figure 3-2: A schematic representation of coalescence, as two droplets merge together and form a larger one\textsuperscript{8}.
It has been demonstrated that increasing electrolyte concentration will inhibit coalescence. There are several theories for the mechanism by which electrolytes limit coalescence. It has been proposed that salt limits the attractiveness of water droplets across the continuous phase, which lowers the rate of coalescence. The characteristic magnitude of the attractive Van der Waals force, \( A \), is:

\[
A = a \frac{(\varepsilon_1 - \varepsilon_2)^2}{(\varepsilon_1 + \varepsilon_2)^2} + b \frac{(n_1^2 - n_2^2)^2}{(n_1^2 + n_2^2)^2} \quad (2)
\]

where \( a \) and \( b \) are constants, \( \varepsilon \) is the dielectric constant of each phase, and \( n \) is the refractive index of each phase. It was argued that since introducing salt raises the refractive index of the aqueous phase, and that organic liquids typically have refractive indices higher than water, the electrolyte acts to match the phases’ refractive indices and minimize the attractive forces. However, this effect is minor for a NaCl system, as even a saturated salt solution’s refractive index is 1.38 (compared to 1.33 for water), and the refractive index of 2-EHA is 1.435. The electrostatic interaction between droplets is also relevant. The droplets of the HIPE system should repel each other electrostatically; the stronger the double layer at the interface, the less likely it is that droplets can overcome the electrostatic repulsion. Therefore another mechanism by which electrolyte might act to stabilize the emulsion is by increasing the strength of the double layer.

An alternative theory to explain this phenomena relies on the electrolyte’s ability to reduce the interfacial tension at the water/oil interface in
the presence of surfactant. It was demonstrated\textsuperscript{2} that this is indeed the case for various electrolytes in a water in mineral oil emulsion, stabilized by glycerol monooleate (Figure 3-3). This reduction in interfacial tension functionally makes the emulsifier better at stabilizing the emulsion, helping to enhance Gibbs elasticity\textsuperscript{10}, which stabilizes droplets against coalescence\textsuperscript{11}.

![Figure 3-3: The interfacial tension of various electrolyte solutions against mineral oil in the presence of emulsifier. Electrolyte effectively reduces the interfacial tension; interestingly, increasing emulsifier increases the interfacial tension\textsuperscript{2}.](image)

The stability of emulsions to temperature is also important for this study, because the elevated temperatures that the emulsions experience while curing can affect their stability. Equation 1 shows that the rate of Ostwald
Ripening is reduced at higher temperatures, which indicates that for HIPE systems, the dominant factor in determining the emulsion stability should be coalescence. As temperature increases in an emulsion, there are two things of interest: the first is that coalescence will happen more rapidly, and the second is that the emulsion will grow further from its phase inversion temperature (PIT; the critical temperature at which emulsions can fluctuate between oil-in-water and water-in-oil emulsions) which affects its stability.

Kabalnov shows\(^{12}\) that the time to complete coalescence, \(\tau\), is:

\[
\tau = \frac{3}{Zd_0^2f} \approx \frac{1}{2d_0^2f} \quad (3)
\]

This equation was developed from a model of the system as monodisperse cubic cells, so \(Z\) represents the coordination number of the cells, \(d_0\) is the initial droplet diameter, and \(f\) is the “frequency of rupture” per unit area. The frequency of rupture can be calculated from:

\[
f = f_0 \exp \left( \frac{-F^*}{k_BT} \right) \quad (4)
\]

From Equation 4, it is clear that the time to complete coalescence is inversely proportion to \(f\), which increases with temperature, and so as temperature increases, the time to complete coalescence decreases (i.e. the rate of coalescence increases).

The phase inversion temperature was demonstrated by Shinoda and Saito empirically and essentially shows that any surfactant can act to stabilize an O/W emulsion or a W/O emulsion. While the concept was originally
demonstrated for emulsions which were stable at room temperature as O/W emulsions\textsuperscript{13}, showing that O/W emulsions would phase invert at high temperatures, Saito and Shinoda later showed that the lower the PIT for a system, the more stable the emulsion would be to kinetic instability\textsuperscript{14}. Furthermore, it was demonstrated that adding a salt to the aqueous phase would decrease the phase inversion temperature\textsuperscript{15}. Kabalnov notes that W/O emulsions are most stable about 20°C above the PIT, after which their stability begins to decrease, likely due to increased coalescence as demonstrated above. Figure 3-4, below, shows how the PIT process works schematically.
3-2 Evaporation in Emulsions

Some samples in this study were also open to the atmosphere when cured, allowing free evaporation of the liquid phases. Both the dispersed and continuous phases could theoretically evaporate; water (B.P. 100°C for pure water) has a much lower boiling point than EHA (B.P. 216°C for EHA) and a comparable one to EGDMA (100°C). Of course, the mixture of

Figure 3.4: A schematic representation of the PIT concept. Emulsions go from O/W to W/O as temperature increases. They pass through the Winsor III state, which is dominated by a surfactant-rich middle phase.
EHA/EGDMA will evaporate much less than the aqueous phase, so water’s evaporation is likely to dominate in the system.

Understanding how water evaporates from an emulsion may be an important part of understanding the properties of poly(HIPE)s allowed to cure while open to the environment. First, it is true that as water evaporates, the system becomes less concentrated and the concentration of electrolyte increases. This will continuously lower the PIT of the system, acting to destabilize it, while also raising its resistance to coalescence, stabilizing it. Assuming, as above, that these effects have different sensitivities to the electrolyte concentration, this means that samples with the same initial concentration of electrolyte cured in different ways (open or closed to the environment) could have very different final properties.

Clint et. al. proposed that there are three steps in water evaporating from an emulsion. First, water droplets must diffuse to the surface of the emulsion. Next, water must “break through” the liquid surface of the emulsion; finally, water must diffuse across a stagnant vapor space. It was demonstrated that the diffusion of water droplets to the surface is the rate-limiting step in this process. The diffusion coefficient according to the Stokes-Einstein equation is:

$$D = \frac{kT}{6\pi \eta r} \quad (5)$$

Where D is the diffusion coefficient, k is Boltzmann’s constant, T is the absolute temperature, and r is the droplet radius. It is also true that in highly concentrated emulsions and at temperatures far from the PIT, this relation is not strictly valid,
for two major reasons. First, in highly concentrated emulsions (i.e. HIPE), the closely clustered droplets form a percolated network (a phenomena in which the droplets are in contact throughout the dispersed phase and the electrical conductivity goes up sharply)\textsuperscript{18}, which enhances the diffusion as a result of deviations from the Stokes-Einstein relation (which assumes non-interacting particles). Secondly, at elevated temperatures, droplets become more attractive and cluster together, reducing diffusion. Still, from this relation it is clear that smaller droplets will preferentially diffuse to the surface of the emulsion in order to evaporate. This may lead to a gradient of droplet diameters in samples where the sample is free to evaporate during curing, which may have an impact on the final mechanical properties of a poly(HIPE) foam.
3-3 Room Temperature HIPE

The properties of HIPE with varying salt concentration were investigated with imaging by optical microscopy (Figure 3-5). Image analysis on these micrographs revealed the droplet size distribution of the room temperature HIPE (Figure 3-6).

*Figure 3-5: Optical micrographs of various HIPEs. Top left, 2% salt; top right, 5% salt; bottom, 7.5% salt. The scale bar is not shown in the final image but is identical to those above.*
Droplet size distributions can demonstrate whether Ostwald ripening or coalescence is dominant in controlling the morphology of a highly concentrated emulsion. The droplet size distribution resulting from Ostwald ripening tends to produce broad tails at the lower end of the droplet size distribution; the opposite behavior is expected for coalescence. The tendency of these distributions to have broad tails at the upper end of the distribution is
evidence that coalescence is the dominant process controlling the stability of these emulsions, even at room temperature.

![Modulus results for samples prepared from various electrolyte concentrations and cured either “covered” (sealed to prevent evaporation) or “uncovered” (freely able to evaporate). Since electrolyte concentration increases if water is allowed to evaporate, the samples are arranged in order of increasing electrolyte concentration. Credit Kristen Rohm and Paul Zackowski for some data collection.](image)

**Figure 3-7:** Modulus results for samples prepared from various electrolyte concentrations and cured either “covered” (sealed to prevent evaporation) or “uncovered” (freely able to evaporate). Since electrolyte concentration increases if water is allowed to evaporate, the samples are arranged in order of increasing electrolyte concentration. Credit Kristen Rohm and Paul Zackowski for some data collection.

### 3-4 Mechanical Testing

A major goal of this work is to understand how electrolyte affects the properties of poly(HIPE) foams, especially their mechanical properties (specifically, Young’s modulus of compression). Additionally, the way that
mechanical properties could be influenced by testing conditions or by post-curing processing was also of interest. Furthermore, as discussed above, the effect of allowing water to freely evaporate from the samples on modulus was explored. The results of mechanical testing on various samples are shown below.

Figure 3-7 clearly shows a drastic increase in modulus for the 5% uncovered samples and the 7.5% covered samples. To either side of these values, the modulus drops. To determine the approximate salt concentration in the samples which were allowed to evaporate, the amount of water which evaporated was measured by weighing the samples before and after curing, and the (average) value of the remaining electrolyte concentration was calculated. Since evaporation preferentially targets small droplets, however, there are likely to be some small droplets with higher concentrations (since losing a small volume of water would increase concentration more rapidly for these small droplets than it would for the large droplets), so the average value is only useful as an approximation.
Thus, the order displayed in Figure 3-7 is in order of increasing electrolyte concentration, though the effect that the process of evaporation has on the morphology of a poly(HIPE) should also be considered. Before discussing why a certain electrolyte concentration has an effect on modulus, it should be considered why the modulus changes between poly(HIPE) samples. There are three possibilities:

1) The salt solution inside a poly(HIPE) plays some role in affecting the modulus.

2) The salt concentration in the HIPE effects the conversion of the poly(HIPE) samples, which in turn effects the modulus of the sample.

3) The salt concentration has an effect on the droplet size (and droplet size distribution) of the emulsion as it cures, resulting in a change in modulus.

<table>
<thead>
<tr>
<th>Initial Salt Concentration (%)</th>
<th>Final Salt Concentration (%)</th>
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<tbody>
<tr>
<td>2</td>
<td>2.3</td>
</tr>
<tr>
<td>5</td>
<td>5.8</td>
</tr>
<tr>
<td>7.5</td>
<td>8.5</td>
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</table>

*Table 3-1: The change in electrolyte concentration from the start of curing to the time samples were removed from the curing bath.*
To determine if the salt solution within the poly(HIPE) had an effect, samples were washed of salt (they were additionally washed of surfactant to determine what effect this had).

Figure 3-8: The measured value of modulus after the samples were washed with water (NaCl extracted) and isopropanol (surfactant extracted). Credit Paul Zackowski.

Figure 3-8 demonstrates that extracted salt from a sample has no effect on its modulus, so this cannot be the source of observed differences in modulus. However, the extraction of surfactant from the sample did produce a
noticeable drop in modulus. The removal of surfactant is associated with the opening on more windows in poly(HIPE) samples, as surfactant can stay in these openings and effectively block them (see Chapter 4). There is an alternative possibility, however, that the change in surface energy owing to the presence of surfactant in

![Graph showing moduli of surfactant-washed solutions stored in water (left) and 10 mM SDS (right).](image)

Figure 3-9: The moduli of surfactant-washed solutions stored in water (left) and 10 mM SDS (right).

the samples led to an increase modulus; for example, it has been shown that a change in surface energy can lead to a change in mechanical properties for
some polymer-based nanocomposites\textsuperscript{19}. To determine this, after washing with water and isopropanol, the aqueous solution was replaced with a 10 mM SDS solution. The mechanical properties of these poly(HIPE)s were compared in Figure 3-9. The interfacial tension of a water/air solution is 72 mN/m, and in a 10 mM solution of SDS/air it is 40 mN/m. Clearly, this change in surface energy has little to no effect on the modulus of a poly(HIPE) sample, demonstrating that the decrease in mechanical properties is accounted for by the opening of more windows in the sample. One alternative possibility is that the struts have decreased in thickness owing to the loss of surfactant (which may have been coating the struts). However, the results of work on fibers in Chapter 4 demonstrate that many windows open upon removal of surfactant, and this should be the dominant mechanism.
Aside from the main question presented above, there is one other interesting source of discrepancy in modulus results. Comparing the values for modulus obtained in Figure 3-7 and 3-8 for 2% NaCl samples, uncovered, the modulus appears to be higher in Figure 3-8 than it is in Figure 3-7. The modulus data in this study was collected by several individuals over a substantial period of time; a review of records revealed that some tests were performed at “high” strain (10 mm/min of compression) and some at “low”
strain (1 mm/min). Samples from the same batch were tested at these different strains; the measured moduli are compared in Figure 3-10.

To determine what effect salt has on the conversion of poly(HIPE), the conversion was determined gravimetrically, based on residual monomer in the samples. Samples were weighed immediately after curing, then washed with water and isopropanol. The isopropanol wash removes both surfactant and residual monomer. Since the weight of salt and surfactant in the sample is known, any additional weight loss is taken as the weight of residual (uncured) monomer. Comparing the uncured monomer to the amount of monomer originally in the sample, a conversion can be calculated.
Figure 3-11: Conversion (as a fraction of residual monomer to original monomer weight) at different curing conditions.

Figure 3-11 indicates that there is not a significant difference in the conversion percentage between different samples, accounting for the experimental error. The error bars on each of the points do not allow confidence that any sample has a markedly different conversion in any of the samples. Thus, the distribution of droplet sizes is likely the controlling factor in the difference in moduli between different samples. To probe the difference in internal morphology, SEM and measurement of the internal surface area were used.
Figure 3-12 shows SEM for each sample. While SEM has sometimes been used for quantitative analysis, it is not likely useful here as such a tool for two major reasons. Firstly, at higher concentrations of internal phase, especially those greater than 90%, the droplet size distribution (and thus the distribution of voids and windows in the sample) becomes too irregular for conventional SEM to probe in a quantitative way. Secondly, SEM can only produce an idea of void distribution over a small piece of a sample, which is not necessarily representative of an entire poly(HIPE) sample. As such, it is more useful to explore the void size distribution with another technique, such as probing the surface area, which is directly correlated to droplet size in an unwashed sample (for the same internal volume percentage, small droplets, which leads to smaller voids, is directly correlated with higher internal surface area). It is also possible that different surface areas can be caused by differing numbers of windows. There are two general reasons why this is considered not to be the case in this work – first, while SEM is not good enough for quantitative determination in this work, Figure 3-12 does allow one to observe that no samples have a markedly different number of windows. Additionally, in an unwashed sample, window opening is driven by the contraction of the oil phase on polymerization, which is not expected to be affected significantly by salt concentration, in contrast with void diameter, which is theoretically closely related to
Figure 3.12: SEM of poly(HIPE) cured at different electrolyte concentrations. (a) is 2% covered, (b) is 2% uncovered, (c) is 5% covered, (d) is 5% uncovered, (e) is 7.5% covered, and (f) is 7.5% uncovered.
The results of physical adsorption tests analyzed by BET theory are presented in Figure 3-13.

*Figure 3-13: The results of physical adsorption tests analyzed by BET for different samples.*

The results presented in Figure 3-13 suggest that there is a correlation between increasing surface area and increasing modulus. Based on the theoretical discussion above about emulsion stability, it appears as though at high temperatures there is a region of higher stability for HIPE around 6-7%. The two major effects that control the stability of the emulsion with increasing electrolyte concentrations are resistance to coalescence (which stabilizes the
emulsion) and a decreasing PIT (which destabilizes the emulsion). These results suggest that the balance between these two effects changes as electrolyte concentration goes up; this is likely because electrolyte does not indefinitely enhance stability to coalescence, but has a point where further electrolyte will no longer stabilize the emulsion further, but the decrease of PIT will continue and act to destabilize the emulsion. The results also suggest that while the emulsion is continually stabilized against coalescence, the effect dominates, leading to a peak value of modulus. The modulus decreases afterwards as the rate of coalescence is no longer significantly affected.
3-5: Conclusions

While traditional understanding of the role of increasing electrolyte concentration in HIPE suggests that emulsions would be continuously stabilized by the addition of salt, the results of this work instead suggest that there is an optimal region of stabilization as electrolyte concentration increases. It is proposed that after a certain concentration of electrolyte, salt no longer continues to stabilize the emulsion against coalescence but it does continue to lower the PIT, which leads to a destabilization of the emulsion. The high temperature stability of the HIPE is reflected in the properties of the poly(HIPE), since its morphology is determined by that of the HIPE. A more stable emulsion has smaller droplets, which leads to smaller voids in the HIPE; based on experimental results, these smaller voids are correlated to higher modulus.
References


van den Tempel, M., Lucassen, J. & Lucassen-Reynders, E. H.  


Chapter 4: Poly(High Internal High Emulsion) Fibers

4-1: Introduction

There are several potential applications for porous, open cell fibers, including encapsulation, controlled release, and reinforcement, but the preparation and processing of such fibers by currently available methods presents challenges. The most common technique for the preparation of such fibers is electrospinning\(^1\), which requires the use of organic solvents. Open cell fibers which could be prepared in more environmentally friendly conditions would be of great utility as a pathway to the aforementioned applications without introducing organic solvent to the process.

Since poly(HIPE) fulfills the morphological criteria (porous, open cell), the possibility of preparing poly(HIPE) fibers has been explored in this work. The possibility is fundamentally based in the idea that the breakup of a stream of fluid through a nozzle into spherical droplets (Rayleigh instability) can be delayed for liquids that have a yield stress\(^2\). Since HIPE present a yield stress, their breakup due to Rayleigh instability should be delayed, and if streams of poly(HIPE) were cured after their ejection, they could cure before the instability, leading to fibers of poly(HIPE). As with traditional poly(HIPE) systems, the extraction of the dispersed phase would lead to a porous, open cell system.

The ability to make these systems is demonstrated and possible modifications, especially to the surface, that the unique curing system allows
(i.e., injecting HIPE into water to cure) have been explored. The process of making fibers and a demonstration that this technique is viable was provided in Chapter 2.
4-2 Effect of Curing Bath Composition

The primary route of exploration in this work is how the morphology of a poly(HIPE) fiber can be manipulated with different curing bath compositions. There are two general directions this work has taken – an exploration of the possibility of interfacial polymerization, where a shell of a different material is grown around the poly(HIPE), and internal phase matching, where salt and initiator in different concentrations were added to the curing bath. First, Figure 4-1 shows the morphology of a poly(HIPE) fiber prepared by injecting the HIPE into deionized water, as a “base” condition. More open surfaces can be obtained by washing the poly(HIPE) fibers with an organic solvent, such as isopropanol or dichloromethane, both of which

Figure 4-1: SEM of a poly(HIPE) fiber. (a) shows a broken fiber’s surface and core; (b) is a closer image of the fibers surface; (c) is a closer image of the fiber core; (d) is a closer image of the surface after washing with dichloromethane. Credit Reza Foudazi for these images.
are used for SEM images.

The surface can be modified from the one presented in Figure 4-1 by manipulating the concentration of the curing bath. As the concentration is varied to different concentrations of salt and initiator, the surface presents

Figure 4-2: The surfaces of fibers prepared in different curing concentrations. Top left is 2% NaCl; top right is 10% NaCl; bottom left is 0.33% NaPS; bottom right is 2% NaCl and 0.33% NaPS.
In general, additions to the curing bath conditions tend to make it more closed off. The addition of purely salt results in a relatively closed surface, though some openings are still visible. The addition of initiator to the bath results in a regular, completely closed surface. The combination of the two conditions leads to a unique morphology that is more open than any other additive condition tested. While it is less open than for fibers cured purely in deionized water, it appears regular and well-ordered in comparison.

In Figure 4-1 the surface of the fiber is still more closed off than the internal structure, likely because the shear forces on the emulsion as it exits the needle cause the droplets to cluster more closely in the center of the volume. The means by which the addition of additives to the curing bath affects the surface is most likely related to firstly the interaction of the boundary of the bath and the emulsion (affecting emulsion properties) and secondly to the interaction of the components of the bath with the polymerization of the fiber. It is possible that osmotic pressures affect the curing of the fibers. In a deionized water bath, there is an inward osmotic pressure from the bath to the fiber; the diffusion of water inward may help keep the surface open. Salt will limit and even reverse this osmotic pressure, which could lead to the more closed surface seen in Figure 4-2. Fibers cured in salt also are observe to contract (that is, their diameters shrink) which could force oil phase to the surface and thus thicken it. Additionally, salt may “slow down” the fiber polymerization. Polymerization in HIPE happens when monomers diffuse into the water droplets and encounter initiator. When a curing bath is present,
however, the monomers will also diffuse outward. This process would inhibit polymerization, since there is no initiator for the monomer to encounter. If polymerization is slower, the closed surface produced by the shear effects may have time to open up again.

The presence of initiator in the bath is likely to both shorten the overall time of polymerization and also cause the polymerization to happen from two directions. Based on the considerations discussed for salt, initiator should also accelerate polymerization because, when monomers diffuse to the bath, they can be radicalized and begin curing. This would lead to a more closed surface. In this case, adding salt would tend to (relatively) inhibit polymerization, since the outward diffusion of monomers would be slower. Still, it should perhaps be expected that a more closed surface should appear for fibers cured in salt and initiator than only in salt, since comparatively the polymerization should be faster. This cannot necessarily be determined by qualitative methods such as SEM, so means of testing the surface properties were used (see below).

The incorporation of an isocyanate in the formulation of the HIPE and a amine-functional compound in the curing bath can lead to a nonporous shell grown around the poly(HIPE). This is distinctly different than what was described above, since with interfacial polymerization the shell is of a different material than the poly(HIPE) core. An overview of this chemical process is shown below.
Figure 4-3: (a) The reaction of isocyanate group of Toluene-2,4-diisocyanate (TDI) and amine group of Diethylenetriamine (DET) forms urea linkage. (b1) The isocyanate group can react with water to form CO$_2$ and an amine functional group, (b2) which can further react with isocyanate to form a urea linkage. Credit Reza Foudazi.

The results of interfacial polymerization using different amine functional compounds are presented as SEM images of the fibers, below.
Figure 4-4: SEM of poly(HIPE) fibers with interfacial polymerization of TDI in the continuous phase of HIPE and (a) DET, (b) PEI1, and (c1, c2) PEI2 in the curing bath. c1 and c2 are at two different magnifications. The inset in c1 represents the open-cell internal morphology of fibers. Credit Reza Foudazi.

The results of Figure 4-4 suggest that interfacial polymerization was a success, particularly when utilizing PEI2 as the amine functional compound.
4.3 Quantitative Analysis of Fiber Surfaces

The first attempt to quantitatively differentiate the fiber surfaces was to study the water evaporation from the fibers. TGA was used below the boiling point of water, and the evaporation of water from the fibers was measured over time.

Figure 4-5: Results of TGA testing according to a heat and hold method. Samples were held at 60°C for approximately one hour. The weight loss is assumed to be water. Some residual monomer may also be evaporating.
The results of Figure 4-5 are not obvious from the graph, because the samples are different weight and dimensions. Calculating the weight loss versus time could provide information about the surface porosity, but it depends on the way that water evaporates from the fibers. It may be that (1) it travels radially outward to the surface to evaporate, but the nature of the sample preparation for TGA testing (i.e. that samples must be small and therefore are either pieces of fibers that broke off naturally during polymerization or were separated from the fiber) may also mean that (2) water travels along the length of the fiber to evaporate. To determine by which means water evaporate, the percentage weight loss versus time of each trial was plotted against the initial weight of the sample. If method (1) is true, then weight loss versus time should be correlated to the diameter of the fiber; if method (2) is correct, then there would be a correlation of weight loss versus time to the length of the sample. Stronger correlation of weight loss versus time to the initial weight of the sample will be indicative of method (2) being correct, since the diameter change from sample to sample is not as significant as the change of length in samples, which is the primary driver of weight change in the samples. Finally, if method (1) is correct, it would also allow determination of information about the surface porosity.
Figure 4-6: A scatter plot of the percentage weight loss versus time against the initial weight of the sample. Samples come from a variety of all curing conditions. There is an obvious strong correlation of the variables.

The strong correlation demonstrated in Figure 4-6 demonstrates that TGA testing with the sample preparation methods used is quite sensitive to the initial weight of the samples. If the sample weight could be strictly controlled it may function as a means to probe sample porosity, but this parameter is difficult to control in practicality. Thus, another method was sought for quantitative analysis.
To better analyze surface porosity, fibers were first prepared from dyed emulsions (HIPE with green food coloring dye incorporated in the aqueous phase) and later, fibers were stored in solutions of the same dyes. The former method would track dye leaving the fibers, and the latter, the dye being absorbed by the fibers. After set periods of time were allowed to pass, the concentration of the dye in the solution was determined with ultraviolet-visible spectroscopy. While it may seem that both methods are equal, there is a critical flaw in the first method, namely that when fibers are prepared for interfacial polymerization, the dye may react. This is demonstrated below. In Figure 4-7, samples were taken from the storage solution in which the fibers were at intervals of 10 minutes and 80 minutes.
Figure 4-7: UV-Vis absorbance of curing bath after polymerization of HIPE fibers containing green food coloring dye in (a) DI-water, (b) 2mg/ml EDDMA in water and (c) 3.5wt% PEI2 in water baths. (d) The difference in the absorbance of curing baths after 80min from time zero. The inset in (d) shows the evolution of the difference in 615-625nm peak from time zero for different curing baths. Credit Reza Foudazi.

In Figure 4-7, there is a clear increase in the concentration of the dye in samples cured in the DI water bath (graph (a)). Likewise, there is a clear though obviously less significant increase for samples cured in 2mg/mL EGDMA (graph (b)). As expected, graph (c) shows almost no change in the
concentration of the dye. It also has an unexpected feature, which is the change in the general shape of the absorbance spectra’s shape. The shifting of the peaks is indicative that part of the dye may have reacted with TDI. As a result, further testing was done by observing the way that dye diffused into the fibers so that it did not have to be incorporated into the emulsion and thus would have no opportunity to react with the TDI.
Figure 4-8: The results of UV-Vis testing on solutions of dye in which fibers at different curing conditions were placed. Samples were taken after absorbing overnight. The scale changes from top to bottom because the stock solution was prepared more strongly.
The results of Figure 4-8 provide a quantitative determination of the surface porosity of the fibers. There is more confidence here that the properties of the surface are being measured, because the samples are whole, unbroken, large fibers. It clearly indicates that fibers cured in deionized water have the most open surfaces; in contrast, fibers cured in 0.33% NaPS have nearly closed surfaces. The other curing conditions present intermediate surface porosities, which is consistent with the SEM images presented above. It also demonstrates that interfacial polymerization to create a core-shell fiber was a success, to provide an alternative route to an open-cell porous fiber with a closed surface.
4-4: Conclusions

The possibility of creating open-cell porous fibers by emulsion templating was explored. The results of the exploration indicate it is very possible to create such fibers and to tune the surface porosity in a variety of ways, from fairly open to completely closed. The most effective means of probing the porosity is likely through an absorption based technique, though supporting with SEM imaging and other means of measuring the transport of matter through the surface can be useful. These fibers could be useful in a variety of applications.
References


Chapter 5: Conclusions and Future Work

5-1: Conclusions

From the results presented in the preceding chapters, an understanding of poly(HIPE) foams and fibers in the context of their structure and properties can be outlined. Firstly, poly(HIPE) foams’ mechanical properties have been found to be correlated to their internal surface area – at least when under the conditions that surface area can be related directly to their internal void diameter. Furthermore, this void diameter has been shown to be related to the electrolyte concentration in the emulsion, but not in a simple fashion – instead, intermediate values of electrolyte lead to minimal void diameters and therefore to higher moduli in foams. This has been suggested to be related to the decreasing influence of the electrolyte’s stabilizing against coalescence while electrolyte continually suppresses the phase inversion temperature of the system, leading to greater high temperature stability for emulsions which are prepared with an aqueous phase having an intermediate electrolyte concentration. This is a valuable understanding for the preparation of foams, as it challenges conventional understanding of the effect of electrolyte on HIPE, which has been thought to act simply as a stabilizer. Going forward, it will be necessary to carefully select electrolyte concentrations to obtain the desired poly(HIPE) properties.

It has been successfully shown that poly(HIPE) fibers can be prepared relatively simply and that their surface properties are tunable by manipulating the properties of the curing bath in which they are made. The otherwise porous fiber can be induced to have a closed surface by introduction of electrolyte or initiator
into the bath; alternatively, a shell of a different material can be grown on the fiber through interfacial polymerization. These preparation techniques will be valuable as further attempts are made to synthesize poly(HIPE) fibers for applications, and the surface porosity can be tuned as needed.

5-2: Future Work

A major potentially interesting avenue of work is to explore how the results of Chapter 3 and Chapter 4 can be combined. For example, what will happen if fibers are polymerized from an emulsion containing 5% salt in the aqueous phase – or any other salt concentration explored above? It may be possible to make higher modulus fibers by this method, and the effect that a different internal concentration may have on the surface porosity remains to be determined. Exploring the ways that different combinations of internal phase chemistries and curing bath chemistries can be used to tune internal fiber morphology and surface porosity could yield exciting and interesting results. Alternatively, explorations of ways in which the results for fiber surface porosity could be obtained for poly(HIPE) monoliths could also be interesting. Traditionally, poly(HIPE) are always cured in sealed media – even the allowance for evaporation in this work is fairly unique. It could be possible to find a way to allow poly(HIPE) monoliths to cure in aqueous media, just like fibers. If so, then the curing bath chemistry could be manipulated to potentially tune the surface properties of monoliths, which could represent a way to create more specialized poly(HIPE).
Focusing on expanding the work without combining the results, monoliths could be further explored by continuing to manipulate their internal phase chemistries. This work could be expanded by changing the concentration of initiator at constant salt concentrations, to see what effect this will have on the final properties. Some tentative experiments have even shown that it is possible to cure poly(HIPE) without a radical initiator. The changing initiator concentration could provide another set of information of how the foam morphology is created – for example, faster cure times may lock in a more stable morphology, and result in better mechanical properties. The types of salts and radical initiators could be changed – it is possible that salts of different charge states (i.e., CaCl₂ and so on) could have different effects – the same could be true of radical initiators with different charge states.

Other considerations could be given to manipulating the continuous phase. Different proportions of monomer and crosslinker – or different kinds of monomers and crosslinkers – would certainly yield varied results. The same series of experiments to test salt concentration could be carried out with a different chemistry of the oil phase, to determine what effect this would have. It is also possible to cure poly(HIPE) with initiator in the oil phase – perhaps this would result in different properties as well.

On fibers, going forward to test possible applications is a good avenue of future research. Seeing how the fibers take up different kinds of impurities from a water solution (such as heavy metals or dispersed particles) would be a step toward exploring their useful properties more. It would also be helpful to find a
way to characterize their mechanical strength; some tentative experiments were done in this direction, but the difficulty of testing the fibers with traditional tensile testing methods presents a challenge. Testing ways that the shells around the poly(HIPE) fibers – whether of the same material or a different one – can be broken or dissolved away would also be of interest.

In summary, there are many possible directions of future research to continue to probe the properties of poly(HIPE) fibers and foams. Finding new ways to manipulate the curing conditions and chemistry, using new post-processing techniques, and testing more relevant properties of the foams and fibers would continue to add to the knowledge and understanding of how to tune and use these systems in future applications.