Hydrophilic Polymeric Adhesives: A Case Study
By Michael Latham

Submitted to the graduate degree program in Bioengineering and the Graduate Faculty of the University of Kansas in partial fulfillment of the requirements for the degree of Master of Bioengineering.

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Chair: Paulette Spencer, D.D.S., Ph.D

Date Approved: December 11, 2020
Abstract

Hydrophilic polymers are key components used in a variety of applications including tissue adhesives, coatings for marine vessels, contact lenses, and drug delivery systems. The ability to use hydrophilic polymers across this spectrum of applications is related, in part, to the opportunity to tune the composition to meet diverse structure and property requirements. As an example, dental adhesives use a combination of hydrophilic and hydrophobic monomers to provide polymers for the repair of damaged tissue, i.e., enamel and dentin. The ratio of hydrophilic and hydrophobic monomers is especially critical since hydrophilicity allows the adhesive to integrate with wet substrates but may leave the adhesive vulnerable to structural degradation due to hydrolytic degradation. The incorporation of the monomer 3-(Trimethoxysilyl)propyl methacrylate (MPS) can theoretically mitigate hydrolytic degradation by creating additional covalent cross links via hydrolysis-condensation reactions.

The objective of this work was to determine the gelation process of hydrophilic polymers containing MPS at varying concentrations. Rheology experiments were planned, but these investigations could not be completed since the lab was shutdown to protect researchers during the COVID-19 pandemic. The investigation was limited to thermal properties and water sorption of polymers with MPS concentrations ranging from 0 to 10 wt% (5.9 mol%). The results revealed statistically significant differences in water sorption and swelling as a function of the MPS concentration. Further analysis revealed that factors such as hydrophilicity, cross-linking density, and solubility contributed to these differences with hydrophilicity playing a dominant role. Future studies should explore the role of MPS in the gelation and durability of formulation in polar solvents.
Acknowledgement

Dr. Paulette Spencer, Dr. Qiang (Charles) Ye, and Dr. Anil Misra for giving me the opportunity to work on this thesis.

Dr. Leon Song for advising me in experimental set up.

Prof. Alvin Beltramo for advising me in statistical analysis

My family for always being there for me

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Introduction

Trauma, age, and disease can damage tissues, limbs, and joints to a level that overwhelms the body’s ability to self-repair. Under these conditions, synthetic, tissue-engineered, and/or hybrid constructs must be used to repair, replace, and restore function to the damaged tissues, limbs, and joints. The repair must meet a variety of criteria including biocompatibility, chemical, physical, and mechanical properties.

Achieving a repair that provides optimum function requires joining dissimilar materials, i.e., the engineered construct must be integrated with the native tissue. The junction between these dissimilar materials is frequently defective and the location where failure initiates. In comparison, interfaces in natural material systems provide superior performance — the rich hierarchical organization of natural material systems is the genesis of extreme and unusual properties including damage tolerance and adaptability. Capturing these capabilities in biomaterials is an ongoing challenge for the biomedical community.

Achieving a seamless, durable interface between the engineered biomaterial and native tissue requires attention to multiple factors including a composition that provides balanced hydrophobicity/hydrophilicity. As an example, PMMA, which is used in bone cements and intraocular lenses, is a hydrophobic polymer with a stable hydrocarbon main chain and ester side groups that can be hydrolyzed. When used as a bone cement, PMMA must fill the spaces between the prosthesis and the surface of the wet tissue.
Hydrophilic characteristics are a two-edged sword, i.e., the ability to thrive in wet environments also leaves polymers vulnerable to hydrolytic degradation. Degradation of the molecular structure through hydrolysis causes polymer breakdown leading potentially to failure of the bone cement and the need for further reconstructive surgeries. One theoretical solution to the weakness of hydrolysis is the incorporation of 3-(Trimethoxysilyl)propyl methacrylate (MPS) into polymer formulations. Similar to monomers such as HEMA and TEGDMA, MPS contains methacrylate groups which are used during curing to form cross links. MPS also possesses multiple methoxy groups which may undergo hydrolysis-condensation reactions in aqueous environments to create additional cross linking (Song L. Q., 2016). The additional cross links can balance the cross links naturally lost to hydrolytic degradation, ensuring the overall structure of a hydrophilic polymer remains intact.

The objective of this work was to determine the impact of MPS incorporation on the gelation process in hydrophilic polymers. The composition of the hydrophilic polymers was relevant to materials used for dental adhesives. Rheology experiments were planned, but investigations could not be completed since the lab was shutdown to protect researchers during the COVID-19 pandemic. The investigation was limited to experiments focusing on thermal properties and water sorption of polymers containing concentrations of MPS ranging from 0 to 10 wt% (5.9 mol%). Point effect sizes with 95% confidence intervals were used in the statistical analysis of the results to determine the magnitude and statistical significance of differences in formulations based on concentration of MPS.
Materials and Methods
Component info

With the exception of MPS and TEGDMA, the hydrophilic polymers used in this study had the same composition. The photo-initiators used in the formulations included 10 [mg] (0.5 wt%) of Camphoroquinone (CQ), 10 [mg] (0.5 wt%) of Ethyl 4-dimethylaminobenzoate (EDMAB), and 20 [mg] (1.0 wt%) of Diphenyliodonium hexafluorophosphate (DPIHP). The composition included 200 [mg] (10 wt%) of 2-methacryloyloxyethyl phosphorylcholine (MPC) and 1560 [mg] (78 wt%) of 2-Hydroxyethyl methacrylate (HEMA). MPC and HEMA were included to give the polymers a resistance to human pathogens and to act as a primer, respectively. Five different ratios of Triethylene glycol dimethacrylate to 3-(Trimethoxysilyl)propyl methacrylate (TEGDMA / MPS) were used to differentiate the formulations: (200/0), (150/50), (100/100), (50/150), and (0/200) [mg/mg]. The formulation containing no MPS acted as the control ("co") and the 4 other experimental, hydrophilic polymers were named based on the weight percentage of MPS ("e2.5", "e5.0", "e7.5", and "e10" respectively).
<table>
<thead>
<tr>
<th>Components</th>
<th>Information</th>
<th>Molecular Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CQ  Camphoroquinone</td>
<td>C_{10}H_{14}O_{2}</td>
<td>MW: 166.22 [g/mol]</td>
</tr>
<tr>
<td>EDMAB  Ethyl 4-dimethylaminobenzoate</td>
<td>C_{11}H_{15}NO_{2}</td>
<td>MW: 193.25 [g/mol]</td>
</tr>
<tr>
<td>DPIHP  Diphenyliodonium hexafluorophosphate</td>
<td>C_{12}H_{10}F_{6}IP</td>
<td>MW: 426.08 [g/mol]</td>
</tr>
<tr>
<td>MPC  2-methacryloyloxyethyl phosphorylcholine</td>
<td>C_{11}H_{22}NO_{6}P</td>
<td>MW: 295.27 [g/mol]</td>
</tr>
<tr>
<td>HEMA  2-Hydroxyethyl methacrylate</td>
<td>C_{6}H_{10}O_{3}</td>
<td>MW: 130.14 [g/mol]</td>
</tr>
<tr>
<td>TEGDMA  Triethylene glycol dimethacrylate</td>
<td>C_{14}H_{22}O_{6}</td>
<td>MW: 286.32 [g/mol]</td>
</tr>
<tr>
<td>MPS  3-(Trimethoxysilyl)propyl methacrylate</td>
<td>C_{10}H_{20}O_{6}Si</td>
<td>MW: 248.35 [g/mol]</td>
</tr>
</tbody>
</table>

*Table 1: Components used in hydrophilic polymer formulations*
The calculated log p values (ratio of solubility in octanol to solubility in water) for each of the monomers and the model adhesive formulations were predicted using ChemBioDraw (BioByte.com). This provides information on the hydrophobic nature of a chemical since the calculated log P value becomes larger as the chemical becomes more hydrophobic (Meylan William M., 2000). Through ChemBioDraw, the calculated log P value for each component of the hydrophilic polymers was calculated by using fragmental additive methods (Meylan William M., 2000). Each monomer is broken up into fragments which contain a non-hydrogen atom as their cores. Each type of fragment is assigned a fragment coefficient value and a correction coefficient. The correction coefficient accounts for the differences between estimated log p values and measured log p values. These values are inserted into the following equation (Leo, 1993):

$$C\log P = \sum F_i a_i + \sum f_j b_j$$  

*Equation 1: Calculated Log P Equation*

Where “F” is the contribution of the fragment type, “a” is the number each fragment occurs, “f” is factors which account for fragment interaction, and “b” is the number of times each factor occurs.

An average ClogP value for each polymer type is generated using the mol average fraction of each component as shown in the equation (Song L. e., 2014) (Parthasarathy, 2012) (Ye, 2011):

$$C\log P_{mol\ avg} = \sum x_i \cdot c\log P_i$$  

*Equation 2: Calculated Log P Molar Average Equation*

Where “x” is the mol fraction for each component and “ClogP” is the ClogP value for each component.
This resulted in the following values for each monomer and polymer composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>ClogP</th>
<th>CO</th>
<th>E2.5</th>
<th>E5.0</th>
<th>E7.5</th>
<th>E10</th>
</tr>
</thead>
<tbody>
<tr>
<td>CQ</td>
<td>1.46</td>
<td>4.45E-3</td>
<td>4.44E-3</td>
<td>4.43E-3</td>
<td>4.42E-3</td>
<td>4.41E-3</td>
</tr>
<tr>
<td>EDMAB</td>
<td>3.12</td>
<td>3.83E-03</td>
<td>3.82E-03</td>
<td>3.81E-03</td>
<td>3.80E-03</td>
<td>3.80E-03</td>
</tr>
<tr>
<td>DPIHP</td>
<td>3.19</td>
<td>3.47E-03</td>
<td>3.46E-03</td>
<td>3.46E-03</td>
<td>3.45E-03</td>
<td>3.44E-03</td>
</tr>
<tr>
<td>MPC</td>
<td>-9.91</td>
<td>5.01E-02</td>
<td>5.00E-02</td>
<td>4.99E-02</td>
<td>4.98E-02</td>
<td>4.97E-02</td>
</tr>
<tr>
<td>HEMA</td>
<td>0.30</td>
<td>8.87E-01</td>
<td>8.85E-01</td>
<td>8.83E-01</td>
<td>8.81E-01</td>
<td>8.80E-01</td>
</tr>
<tr>
<td>TEGDMA</td>
<td>1.86</td>
<td>5.17E-02</td>
<td>3.87E-02</td>
<td>2.57E-02</td>
<td>1.28E-02</td>
<td>0</td>
</tr>
<tr>
<td>MPS</td>
<td>1.30</td>
<td>0</td>
<td>1.49E-02</td>
<td>2.97E-02</td>
<td>4.44E-02</td>
<td>5.91E-02</td>
</tr>
<tr>
<td>Total Avg. ClogP</td>
<td>-1.02E-01</td>
<td>-1.06E-01</td>
<td>-1.11E-01</td>
<td>-1.15E-01</td>
<td>-1.20E-01</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Average Calculated Log P Values for Hydrophilic Polymer Formulations

As seen from Table 2, a polymer becomes more hydrophilic as the mol percentage of MPS increases and TEGDMA decreases. However, the greatest difference in average ClogP values is only 1.79E-2 which is due to the similarity in composition between formulations.

Sample Preparation

The hydrophilic polymers were made at room temperature (25 [C]) under amber light to avoid uncontrolled photopolymerization. The containers for the chemicals 2-Hydroxyethyl methacrylate (HEMA), 3-(Trimethoxyxisy)l propyl methacrylate (MPS), Triethylene Glycol Dimethacrylate (TEGDMA), 2-methacryloyloxyethyl phosphorylcholine (MPC), Camphoroquinone (CQ), Ethyl 4-dimethylaminobenzoate (EDMAB), and Diphenyliodonium hexafluorophosphate (DPIHP) were removed from a refrigerator and allowed to reach room temperature. After 30 [min], a piece of parchment paper was placed on a Mettler Toledo XS 205
Dual Range balance and the mass was zeroed. Using a clean, metal spatula, CQ was placed on
the parchment paper until the digital balance read 10 [mg] (0.5 wt %) and the mass was recorded.
This process was repeated with 10 [mg] of EDMAB (0.5 wt %) and 20 [mg] of DPIHP (1 wt %)
and all 3 components were placed in a clean, brown vial. The brown vial containing CQ,
EDMAB, and DPIHP was placed directly on the digital balance and the mass value was zeroed.
200 [mg] (10 wt %) of MPC was added directly to the brown vial to avoid excessive atmospheric
exposure. The mass of the MPC was recorded. Using a disposable pipette, 1560 [mg] (78 wt %)
of HEMA was added to the brown vial and the mass was recorded. The sealed vial was placed on
a Vortex Maxi Mix 2 for 30 sec to allow the components to fully mix. After mixing, the brown
vial was placed back on the digital balance, and the autopipette was used to add 200 to 0 [mg]
(10 to 0 wt%) of TEGDMA to the vial depending on the formulation. The mass of TEGDMA
was recorded.

The vial was sealed and placed on the Vortex Maxi Mix 2 to ensure the dissolution of the
TEGDMA. This was confirmed visually by checking every 10 [sec] if precipitates remained in
the brown vial. Once no more precipitates were visible, the vial was placed in a Titer Plate
Shaker 4625 (Thermo Scientific Barnstead) for 30 min to ensure complete mixing of the
components. After 30 [min], the cap was removed, and the vial was placed on the digital balance
which was then zeroed. Using an autopipette, 0 to 200 [mg] (0 to 10 wt%) of MPS was added
depending on the formulation. The mass of MPS was recorded and the brown vial was sealed
and returned to the Titer Plate Shaker 4625 (Thermo Scientific Barnstead) for 2 [hours]. This
process was repeated to create 2000 [mg] (100 wt %) of each of the 4 experimental polymer
types.
All cured polymer samples were made using the same process regardless of polymer type. An automatic pipette was used to place 24 [μL] of hydrophilic polymer was placed in a Hermetic Lid. The lid filled with hydrophilic polymer was covered with a coverslip to reduce air which interferes with the photopolymerization. The sample was photocured using a halogen curing light (Spectrum 800; Dentsply, Milford, DE) at an irradiance of 550 [mW/cm²], 470 [nm]) for 40 [sec] at a distance of 2 [cm] from the sample. After photocuring, the sample was stored under yellow light for 48 [hours] to allow time for dark cure. At 48 hours, the sample was removed from the lid. The dimensions of the sample were as follows: diameter of about 40 mm and height of 2.1 mm.
### Composition of Formulations

<table>
<thead>
<tr>
<th>Formula Name</th>
<th>CO</th>
<th>E2.5</th>
<th>E5.0</th>
<th>E7.5</th>
<th>E10</th>
</tr>
</thead>
<tbody>
<tr>
<td>CQ</td>
<td>10 [mg] (0.5 wt%)</td>
<td>10 [mg] (0.5 wt%)</td>
<td>10 [mg] (0.5 wt%)</td>
<td>10 [mg] (0.5 wt%)</td>
<td>10 [mg] (0.5 wt%)</td>
</tr>
<tr>
<td>EDMAB</td>
<td>10 [mg] (0.5 wt%)</td>
<td>10 [mg] (0.5 wt%)</td>
<td>10 [mg] (0.5 wt%)</td>
<td>10 [mg] (0.5 wt%)</td>
<td>10 [mg] (0.5 wt%)</td>
</tr>
<tr>
<td>DPIHP</td>
<td>20 [mg] (1.0 wt%)</td>
<td>20 [mg] (1.0 wt%)</td>
<td>20 [mg] (1.0 wt%)</td>
<td>20 [mg] (1.0 wt%)</td>
<td>20 [mg] (1.0 wt%)</td>
</tr>
<tr>
<td>MPC</td>
<td>200 [mg] (10 wt%)</td>
<td>200 [mg] (10 wt%)</td>
<td>200 [mg] (10 wt%)</td>
<td>200 [mg] (10 wt%)</td>
<td>200 [mg] (10 wt%)</td>
</tr>
<tr>
<td>HEMA</td>
<td>1760 [mg] (78 wt%)</td>
<td>1760 [mg] (78 wt%)</td>
<td>1760 [mg] (78 wt%)</td>
<td>1760 [mg] (78 wt%)</td>
<td>1760 [mg] (78 wt%)</td>
</tr>
<tr>
<td>TEGDMA</td>
<td>200 [mg] (10 wt%)</td>
<td>150 [mg] (7.5 wt%)</td>
<td>100 [mg] (5.0 wt%)</td>
<td>50 [mg] (2.5 wt%)</td>
<td>0 [mg] (0 wt%)</td>
</tr>
<tr>
<td>MPS</td>
<td>0 [mg] (0 wt%)</td>
<td>50 [mg] (2.5 wt%)</td>
<td>100 [mg] (5.0 wt%)</td>
<td>150 [mg] (7.5 wt%)</td>
<td>200 [mg] (10 wt%)</td>
</tr>
<tr>
<td>Total</td>
<td>2000 [mg] (100 wt%)</td>
<td>2000 [mg] (100 wt%)</td>
<td>2000 [mg] (100 wt%)</td>
<td>2000 [mg] (100 wt%)</td>
<td>2000 [mg] (100 wt%)</td>
</tr>
</tbody>
</table>

Table 3: Composition of Hydrophilic Polymer Formulations

#### Experiment procedures

**FTIR Test Procedure**

An infrared (IR) spectrometer (Spectrum 400 Fourier transform infrared spectrophotometer; Perkin-Elmer) equipped with an attenuated total reflectance (ATR) accessory (PIKE Technologies Gladi-ATR, Madison, WI) was used to monitor the change in chemical composition of the hydrophilic polymer as it is photocured. The spectrometer was set to scan across a range of 4000-650 [cm\(^{-1}\)] for 20 [min] with a spectral resolution of 4 [cm\(^{-1}\)]. A drop of liquid resin was placed on the ATR crystal and the sample was covered with a coverslip to reduce oxygen. Oxygen will inhibit the photopolymerization process. After 30 IR spectra of the uncured polymer was recorded as a base value, the uncured polymer was photocured using a halogen curing light (Spectrum 800; Dentsply, Milford, DE) at 550 [mW/cm\(^2\)] for 40 [sec] with the light placed within 2 [cm] of the polymer on the ATR crystal. Once the scan was completed, the ratio of the absorbance at 1636 [cm\(^{-1}\)], representing C=C bonds, was compared to the
absorbance at 1710-1720 [cm⁻¹], representing C=O bonds, since the absorbance at 1636 [cm⁻¹] should decrease as the alkenes are used in photopolymerization while the absorbance at 1710-1720 [cm⁻¹] should remain unchanged, providing a basis to compare the absorbance at 1636 [cm⁻¹] to. These ratios were used to calculate the degree of conversion (DoC) for the hydrophilic polymer.

\[
DoC = \left(1 - \left(\frac{Absorbance_{\text{postcure}}^{1636 \text{ cm}^{-1}}}{Absorbance_{\text{postcure}}^{1710-1720 \text{ cm}^{-1}}} \frac{Absorbance_{\text{precure}}^{1636 \text{ cm}^{-1}}}{Absorbance_{\text{precure}}^{1710-1720 \text{ cm}^{-1}}}\right)\right) \times 100\%
\]

*Equation 3: Degree of Conversion [%] Equation*

The calculated DoC for the last 30 IR spectra was used to obtain an average DoC for the polymer. This process was repeated so that 3 average DoC were obtained for each polymer, resulting in a total of 15 averages.

**Thermal Degradation Experiment Procedure**

Thermal degradation was assessed using thermogravimetric analysis through a PYRIS 1 Thermogravimetric Analyzer (TGA) (PerkinElmer, Akron, OH, USA). A 3-4 [mg] fragment was cut from a photocured polymer sample using a razor blade and weighed using a Mettle Toledo XS 205 Dual Range balance with up to 0.01 [mg] resolution for efficiency. Once it was confirmed that the sample was within the acceptable mass range, the sample was stored in a 1.5 [mL] centrifuge capsule with resealable lid until use. An aluminum pan was placed inside a ceramic container and hung from the wire in the TGA. The furnace tube was raised and sealed shut for 5 [min] to allow the mass of the ceramic container and aluminum pan to reach equilibrium after which their combined mass was set as the zero weight in the program. When the furnace tube is sealed shut, nitrogen gas (30 [mL/min]) is automatically pumped through the
tube to purge oxygen and therefore limit possible oxidation of the sample during testing. The furnace tube was then lowered, and the ceramic container and aluminum pan were removed from the wire using tweezers. The 3–4 [mg] fragment was taken from its capsule and placed inside the aluminum pan in the ceramic container. The ceramic container, now containing the fragment, was returned to the wire and the furnace tube was resealed. The combined mass was allowed 5 [min] to reach equilibrium after which the detected mass was set as the sample weight. The TGA was then set to perform the following test:

1. expose the sample to 50 [C] for 1 [min]
2. increase the temperature from 50 [C] to 600 [C] at 20 [C/min]
3. lower the temperature from 600 [C] to 50 [C] at 50 [C/min]

During this entire process, the TGA recorded the mass of the polymer fragment [%] vs. temperature [C]. The temperature at which 5% of the mass of the sample was lost was determined from the plot and recorded for each sample tested. This was repeated so that data on 3 samples for each polymer was collected for a total of 15 data points. After confirming each group in the data set fulfilled the normality of distribution and the homogeneity of variance assumptions through a Shapiro-Wilk test and a Brown-Forsythe test, respectively using an alpha of 0.05; a Hedge’s D point effect size with a 95% confidence interval was generated between the control polymer (co) and each of the other experimental polymers for a total of 4 point effect sizes and confidence intervals.

**Thermal Glass Transition Experiment Procedure**

Thermal based testing was performed using a TA instruments model Q200 modulated differential scanning calorimetry (MDSC) to determine the glass transition temperature of the polymers. Two Tzero aluminum pans each sealed with a Tzero lid were placed in the MDSC,
one to hold a photocured sample during testing and the other to act as a reference point for heat flow calculations. The MDSC test was set up to first equilibrate a sample at -40 [C] for 1 [min]. The sample was then heated at a rate of 3 [C/min] to 200 [C] all the while running a secondary modulating ramp at ± 2 [C/min] so that the reversible heat flow and non-reversible heat flow signals could be separated. Once the sample reached a temperature of 200 [C], the sample was then cooled to -40 [C] at the same rates at which it was heated. With the first cycle of heating and cooling removing any thermal history that may have developed during the creation of the samples, the heating and cooling cycle was repeated and the heat flow [W/g] vs temperature [C] was recorded. Throughout the entire testing process, the MDSC cycled in nitrogen gas at a rate of 50 [mL/min] to prevent possible reactions with oxygen as the sample was heated and cooled.

When the test was complete, the reversible heat flow data for the 2nd cycle of heating and cooling was analyzed to obtain the thermal properties such as the thermal glass transition temperature, the range of temperature over which the phase transition between glassy and rubbery states occurred, and the change in reverse heat flow signal as the polymer transitioned between a glassy and rubbery state. This was repeated 3 times per polymer type for a total of 15 data sets.

After confirming the data collected from the experiment on the thermal glass transition temperature, the reverse heat flow signal change due to phase transition (referred to as the signal change value), and the temperature range over which the transition between glassy or rigid and rubbery characteristics occurred (referred to as the temperature range value) fulfilled the normality of distribution and the homogeneity of variance assumptions through multiple Shapiro-Wilk and Brown-Forsythe tests, respectively using an alpha of 0.05, a Hedge’s D point effect size with a 95% confidence interval was generated by comparing the average thermal
properties of the control polymer (co) with each of the other experimental polymers for a total of 4 effect sizes and confidence intervals for each thermal property of interest.

**Water Miscibility Experiment Procedure**

To determine the miscibility of a polymer in water the amount of water required for miscibility to occur was investigated. This was done by first placing a brown, glass vial on a balance and zeroing the balance. Using a disposable pipette, 400 [mg] of liquid resin was placed in the vial with 80 [mg] of deionized water (DIH$_2$O). After recording the weight of the liquid resin and DIH$_2$O in the vial and zeroing out the balance (0.01 [mg] resolution, Mettler Toledo, XS 205 Dual range, Columbus, OH), 10 [mg] of DIH$_2$O was added to the vial. The vial was inspected to determine if a homogeneous mixture had been formed. The process of recording, zeroing, adding 10 [mg] of DIH$_2$O, and gently shaking was repeated until turbidity was visually noted in the vial. Once turbidity was visually indicated, the weight percentage of water within the liquid resin-DIH$_2$O mixture was calculated and recorded as “w1”. The process was repeated with the same liquid resin-DIH$_2$O combination except increments of 10 [mg] of liquid resin was added rather than DIH$_2$O until there was no longer a turbid appearance within the glass vial. The weight percentage of DIH$_2$O at this point was calculated and recorded as “w2”. The weight percentages of DIH$_2$O expressed in w1 and w2 were then averaged to obtain the average weight percentage of DIH$_2$O required for miscibility in water to occur. This was repeated for all remaining hydrophilic polymer formulations for a total of 10 measurements across all 5 hydrophilic polymers. Statistical analysis was not performed due to low sample size for each hydrophilic polymer.

**Solubility and Water Sorption Experiment Procedure**

For the water testing, 5 samples of each hydrophilic polymer (total of 25 samples) were created, weighed using a Mettler Toledo XS 205 Dual Range Balance with a resolution of 0.01
[mg], and recorded as “M0” to represent the masses of each sample prewashing. Each sample was placed in a labeled 1.5 [mL] centrifuge capsule with a resealable lid to act as its container for the remainder of the water-based testing. Each capsule was then filled with 1.5 [mL] of DIH₂O, sealed shut, and placed in a Thermo Scientific Lindberg Blue M Convection Oven at 37 [C] for 7 days. Every 24 hours, all of the capsules were removed from the convection oven, the DIH₂O was drained from each capsule and replaced with fresh DIH₂O, resealed, and placed back in the convection oven at previous settings. After 7 days, the capsules were then drained of their DIH₂O and placed unsealed in the convection oven at 37 [C] for 2 days for initial drying. The unsealed capsules containing the samples were removed from the convection oven and placed in a Fisher Scientific Isotemp Model 282A Vacuum Oven at 37 [C] which was purged to an atmospheric pressure of 0.1 [in of Hg] by a Welch DuoSeal 1376 Vacuum Pump to ensure the samples were fully dried. Every 48-72 hours depending on scheduling, the samples were removed from the vacuum oven, the samples were weighed, the mass was recorded, and the samples were returned to the vacuum oven at the previous settings. This process continued until there was less than or equal to 0.1 [mg] difference between the current and previous mass measurement across all 25 samples, which was the criteria for dryness for the experiment. Although the samples reached this point after 13 [days], the samples were kept in the vacuum oven at 37 [C], 0.1 [in of Hg] for an additional 4 days, a total of 17 days, due to scheduling conflicts. The masses after 17 [days] of being kept on the vacuum oven at 37 [C], 0.1 [in of Hg] were labeled as “M1” and the swelling phase began directly afterwards.

For the swelling phase, each capsule containing a sample was refilled with 1.5 [mL] of DIH₂O, sealed, and placed inside the convection oven at 37 [C]. The process for monitoring the change in mass of the polymers as they swelled involved removing the samples from the
convection oven, unsealing and draining all 25 capsules, weighing each sample, recording the masses, placing each sample back into its capsule with a fresh supply of 1.5 [mL] of DIH₂O, and placing the resealed capsules back into the convection oven at 37 [C]. This occurred 3, 5, 12, 24, 48, and 96 [hours] after taking the “M1” measurement with the masses at 96 [hours] labeled as “M2”.

The 3rd and final phase of the absorption experiment consisted of a final drying phase. The capsules containing the 25 swollen samples were removed from the convection oven and drained the 1.5 [mL] of DIH₂O from each capsule. The samples were returned to their capsules and the unsealed capsules were placed in the convection oven at 37 [C] for 7 days. After 7 days of drying in the convection oven, the capsules were transferred to the vacuum oven at 37 [C], 0.1 [in of Hg] until the criteria for dryness was met. Mass values were measured every 2 days until the criteria was fulfilled by day 6 in the vacuum oven. The mass values at day 6 were labeled as “M3”.

Using the masses labeled “M1”, “M2”, and “M3”, water absorption-based properties such as solubility and water sorption were calculated using the following equations:

\[
Solubility \ [\%] = W_{sol} = \left( \frac{M_1 - M_3}{M_1} \right) \times 100 \ [%]
\]

\textit{Equation 4: Solubility [%] Equation}

\[
Sorption \ [\%] = \left( \frac{M_2 - M_3}{M_1} \right) \times 100 \ [%]
\]

\textit{Equation 5: (Water) Sorption [%] Equation}

Using the solubility and sorption values calculated for each sample, average values with standard deviations were calculated for each hydrophilic polymer. This was followed by determining the Hedge’s d point effect size with 95% confidence intervals between the control
and the 4 experimental hydrophilic polymers after proving that the results fulfilled the required assumptions of normality of distribution through Shapiro-Wilk tests and homogeneity of variance through Brown-Forsythe tests.

**Swelling Equilibrium, Swelling Rate, and Density Experiment Procedure**

All 25 samples, 5 per hydrophilic polymer, were taken directly from the end of the Water Sorption Experiment. To ensure that the moisture was removed prior to the swelling experiment, the 25 samples were placed in their labeled capsules unsealed in a Fisher Scientific Isotemp Model 282A Vacuum Oven at 37°C, purged to an atmospheric pressure of 0.1 [in of Hg] using a Welch DuoSeal 1376 Vacuum Pump until all 25 samples reached a constant mass value. This point was identified by weighing each sample using a Mettler Toledo XS 205 Dual Range Balance every 2 days. The mass was recorded, and the samples were returned to the vacuum oven at the previous temperature and atmospheric settings. If the difference in mass values between the current and previous mass values across all 25 samples was less than or equal to 0.1 [mg], the samples were identified as having a constant mass value. This was reached by day 6 in the vacuum oven. The mass values at day 6 were labeled as the “M0” values and indicated the mass at which a sample was fully dry.

Next, the mass in air and mass in water for each sample was determined. For this experiment the Mettler Toledo XS 205 Dual Range balance was modified with an XPR/XSR Analytical Density Kit which allowed the mass of a sample to be measured when dry (Mₐ) and when submerged in a small container of DIH₂O (Mₜ). The process for a single measurement was as follows: water was drained from the sample vial, the sample was patted dry using a kimwipe, Mₐ for the sample was determined and recorded. The sample was submerged in the small container of DIH₂O and Mₜ was determined and recorded. Mₜ was determined within 10 [sec] to
avoid additional swelling during the measurement process. Finally, the sample was returned to its original container which was then refilled with 1.5 [mL] of DIH₂O and sealed. This entire process was performed under 2 minutes so as to avoid significant differences in time exposure to water between sample measurements. This process was repeated with every sample after 1, 3, 5, 10, 24, 48, and 72 hours of swelling in DIH₂O. In between measurements, all 25 samples were stored at room temperature under yellow light to avoid additional photopolymerization. Swelling properties such as volume, volume ratio, and density of each sample was determined using the following equations:

\[
Volume = \alpha \times \frac{(M_a - M_w)}{\rho_{DIH2O} - \rho_{air}}
\]

\[
Swelling \text{ } Ratio = \left(\frac{V_{current}}{V_0} - 1\right) \times 100\%
\]

*Equation 6: Swelling Ratio Equation*

\[
Density = \left(\frac{M_{a,hour \_0}}{M_{a,hour \_0} - M_{w,hour \_0}}\right) \times (\rho_{DIH2O} - \rho_{air}) + \rho_{air}
\]

*Equation 7: Density Equation*

Ma is the mass in air, Mw is the mass in water, \( \rho_{DIH2O} = 1 \) [g/cm^3] is density of water, \( \rho_{air} = 0.0012 \) [g/cm^3] is density of air, and alpha (\( \alpha \)) = 0.99985 is a factor to account for buoyancy on the sample created by air.

The density was calculated using the mass values at 0 hours of submergence in DIH₂O. Over time, the samples will swell to contain DIH₂O so density values calculated beyond hour 0 would reflect the mass and volume ratio of the polymer and DIH₂O combination rather than the pure polymer.

After using the volume values for each sample to determine the swelling ratio, the data were analyzed statistically. Within each hydrophilic polymer, the swelling ratio data at each hour
interval was compared to the swelling ratio data of the next interval to determine how these values changed with time. Point effect sizes with a magnitude of at most ±0.07 were considered to represent swelling equilibrium since the magnitude shows that the standardized mean values exist within a 5% ranged interval, or ±2.5%, of each other. Comparisons were made between polymer types based on points of interest that were revealed during detailed analysis of the results. All of the statistical analysis was performed after determining that the data sets fulfilled the required assumptions through Shapiro-Wilk and Brown-Forsythe tests.

**Gel Fraction Experiment Procedure**

For the gel fraction experiment, 3 cured samples for each hydrophilic polymer were prepared for a total of 15 samples. Each sample’s mass was weighed using a Mettler Toledo XS 205 Dual Range Balance and that value was used as a baseline value before washing (M0).

Each sample was place in an individual glass vial with a resealable lid. The vial was filled with 20 [mL] of 90% ethanol, sealed, and stored in Thermo Scientific Lindberg Blue M Convection Oven at 37 [C]. The ethanol was replaced every 24 hours for a total of 7 days. After 7 days, all capsules were drained of ethanol and all samples were patted dry using a kim wipe. The samples were weighed using the digital balance and the mass was recorded. The samples were then returned to their capsules and placed unsealed in a Fisher Scientific Isotemp Model 282A Vacuum Oven at 37 [C] purged to 0.1 [in of Hg] by a Welch DuoSeal 1376 Vacuum Pump. Every 24 hours for 7 days, the samples were removed from the vacuum oven, the mass was determined and recorded, and the samples were returned to the vacuum oven at previous settings. Due to the slow evaporation rates and multiple hydrophilic polymers showing solvent retention, the samples were placed back in the vacuum oven at previous settings and mass
measurements were made and recorded 13 and 15 days after the 7\textsuperscript{th} day of drying. The gel fraction value for each sample for each day was then calculated using the following equation:

\[
Gel\ Fraction\ [\%] = \left( \frac{M}{M_0} \right) \times 100\%
\]

\textit{Equation 8: Gel Fraction [\%] Equation}

Where “M0” represents the mass of the sample before the ethanol washing process (day - 7) and “M” represents the mass of the sample as it dries. The gel fraction values were used to obtain an average gel fraction with standard deviation for each experimental hydrophilic polymer on each day of the experiment. The results were analyzed statistically to compare the time required to reach consistent average gel fraction values. The procedure for the statistical analysis was as follows: a Hedge’s d point effect size with 95\% confidence interval was created to compare the average gel fraction values of a day with the previous day’s values within each hydrophilic polymer. Consistent values would be indicated by a point effect size being within a range of \(\pm 0.07\) or a day’s average gel fraction value being greater than only the bottom 47.5 to 52.5\% of gel fractions values from the population of the previous day’s gel fraction values. Comparisons between hydrophilic polymers were made depending on key events revealed by the interval plot. The statistical analysis was performed after confirming required assumptions such as normality of distribution for each group (hydrophilic polymer-day combination) and sphericity and homogeneity of variance for the tests where the comparisons were within or between hydrophilic polymers respectively.

\textbf{Importance of Experimentation}

\textbf{Importance in Degree of Conversion Experimentation}

The degree of conversion reveals information relevant to the final physical, mechanical, and biological properties of the polymer (Galvão, 2013). As the degree of conversion increases,
more of the material is able to react and form cross links with other monomers which can lead to the formation of long polymer chains or cross-linked networks which impact structural properties such as swelling and elasticity (Brazel, 2012). Low degrees of conversion may leave leftover monomers which can leach from the polymer and cause a loss of structural integrity, biological damage in the form of providing sites for protein and bacteria attachment, biofilm formation. The leached monomers may also cause cytotoxic responses at the polymer/tissue interface (Willey, 2009).

**Importance of Thermal Based Experimentation**

Understanding thermal properties can reveal information about structural changes that may occur in a polymer with simple decreases or increases in temperature. In the same system, thermal energy will be spontaneously transferred from hotter to colder bodies in order to obtain thermal equilibrium (Atkins, 2010). With the influx of additional energy, portions of the molecular structure may be able to overcome weaker bonding, such as Van der Waals forces or hydrogen bonding — this can lead to increased mobility in the polymer chains (Brazel, 2012). The mobile polymer chains will dissipate energy rather than elastically responding to it, causing an increase in the flexible or rubbery characteristics of the polymer. If the influx of thermal energy is great enough, organized regions may be disrupted causing a rubbery polymer to melt and obtain liquid-like properties or main chain scission, also known as thermal degradation. The results can be reversed if a polymer is placed in a colder environment. As heat spontaneously leaves the polymer, chains can lose enough energy that they can no longer overcome secondary forces within the molecular structure, causing a polymer’s structure to transition from liquid to rubbery to glassy state.
This is important to know because when polymers are designed or chosen to be used in a certain task, it often requires the polymer to express specific properties and therefore specific structural characteristics. If a polymer changes from a glassy to a rubbery structure or vice versa when it is used in a specific application, dangerous consequences can occur. One example is the impact of cold temperatures on the structure of the O-rings on the space shuttle Challenger, leading to its explosion during launch (Tomsen, 2017).

Although changes in temperature can impact the structure of a polymer, the degree of the impact is dependent on many other properties, such as molecular weight, cross linking density, and homogeneity (Brazel, 2012). Thus, thermal properties can reveal important information about polymer structure.

**Importance of Aqueous Based Experimentation**

Polar solvents such as water can impact the properties of hydrophilic polymers. Water is a small molecule consisting of only 1 oxygen atom and 2 hydrogen atoms, but the dipole-dipole interaction between the oxygen and the hydrogens makes water a very polar molecule. This allows water to act as a plasticizer, easily infiltrating the hydrophilic polymer network and disrupting secondary bonds — this activity can lead to dramatic changes in properties (Brazel, 2012).

One such change is to the shape of the hydrophilic polymer (Brazel, 2012). As the solubility parameters between water and the hydrophilic polymer become more similar, interactions between the solute and solvent are encouraged. This causes an increase in the available free volume allowing polymer chains to uncoil which encourages more solute-solvent interactions. These events can lead to the dissolution of linear or branched polymers.
Crosslinked hydrophilic polymers, such as dental adhesives, do not generally dissolve since the plasticizing effect of water is unable to overcome the covalent bonds created from crosslinking. As opposed to dissolving, crosslinked hydrophilic polymers can swell to accommodate more water (Brazel, 2012). However, hydrophilic polymers may be vulnerable to hydrolysis so even covalent bonds formed during crosslinking may degrade with time. Degradation changes the structural and thermal properties of the polymer since chain mobility is now easier, encouraging lower thermal glass transition temperatures and more rubbery characteristics.

Swelling will change the volume and shape of the hydrophilic polymer. Depending on the application, swelling may be a desirable trait, e.g., some investigators claim that swelling can counter the stress associated with polymerization shrinkage of dental adhesives. Another potential advantage associated with swelling is the release of unpolymerized components. As the hydrophilic polymer expands, it increases the available free volume leading to space for polymer chain mobility. Unpolymerized monomer or oligomer that was once trapped within the crosslinked polymer may now be mobilized — this activity can lead to reactions that may alter the properties of the hydrophilic polymer. The unreacted components may also leave the network and enter the surrounding micro-environment. Once again, depending on the application this may lead to detrimental outcomes including cytotoxic responses in the tissue (Abedin F. Q., 2014) (Abedin F. Q., 2015).

Determining the impact that water has on a hydrophilic polymer reveals important information about structure and properties. For example, the interaction between the hydrophilic polymer and water can reveal information about the crosslink density, hydrophilic/hydrophobic balance, unreacted components, and functionalities that may be vulnerable to hydrolytic
degradation. This information can be central to determining if the hydrophilic polymer will meet the needs associated with a particular application.

**Importance of Rheological Based Experimentation**

“In a traditional sense, engineers typically deal with elastic solids and viscous fluids as two separate and distinct classes of materials” (Brazel, 2012). Elastic materials, such as steel, are known as “linear elastic or Hookean solid” (Brazel, 2012). This type of material is represented by a spring due to the elastic nature of the material which “snaps back to its original length after the strain is removed” (Brazel, 2012). These materials are often represented by Hook’s law which shows a linear relationship between stress and strain for elastic materials.

\[
\tau = G \gamma
\]

*Equation 9: Hook's Law*

On the other hand, some materials are classified as viscous materials. Viscous materials, such as water, are represented by a dashpot due to how these “linear viscous or Newtonian fluid” materials follow Newton’s law which shows the direct relationship between stress and the strain rate rather than strain (Brazel, 2012).

\[
\tau = \eta \dot{\gamma}
\]

*Equation 10: Newton's Law of Viscosity*

The rate dependency of viscous materials causes them to rely more on time in order for various physical parameters to affect the system unlike the instantaneous, elastic counterparts. However, these purely elastic and viscous materials are the end points of a spectrum of materials which express both elastic and viscous properties. Within this third “Viscoelastic” classification are polymers due to how they can possess a diverse ratio of elastic and viscous properties and how this ratio can change in response to external and internal factors. The mixture of elastic and
viscous properties means that using Hook’s or Newton’s laws alone when investigating the properties of viscoelastic materials may provide misleading, inaccurate, or non-reproducible information. This can lead to viscoelastic materials being used inappropriately or used when they cannot meet the needs associated with a particular application.

The properties of viscoelastic polymers can be investigated through rheology: “the science of the deformation and flow of materials” (Brazel, 2012). Rheological concepts can accomplish this by recognizing the common factor between elastic and viscous materials: applied force. Although elastic portions react instantaneously and viscous portions have a delayed reaction to applied forces, both responses require an initial applied force. Therefore, by monitoring how a material responds to an applied shear stress or strain, one can determine not only where a material lies on the viscoelastic spectrum, but also internal properties and limits which influence the overall structure.

Key properties

Key Thermal Based Properties

Two specific areas to investigate when exploring how the structure of a material changes with temperature are 1) the transition between a glassy or rigid state and a rubbery state and, due to the cross-linking of the hydrophilic polymers being examined, 2) thermal degradation.

Transition between elastic and rubbery phases

The transition between a rigid or glassy state and a rubbery state is a highly informative section on the internal properties of any polymer. This is because a diverse set of information can be obtained from simply monitoring 3 specific portions of this phase transition.

The first portion is the location of the Glass Transition Temperature (Tg). The thermal glass transition temperature marks the temperature at which a material has been considered to
transition between the rigid or glassy state and a rubbery state (Brazel, 2012). This is an especially key piece of information since this property identifies the temperature range for the polymer. The thermal glass transition temperature is also influenced by a variety of factors such as the available free volume, attractive forces between molecules, and the internal mobility, stiffness, and length of polymer chains, allowing for the optimization of thermal properties by modifying a polymer’s components. The number of glass transition temperatures in a material provides insight on polymer chain composition within a material (Brazel, 2012). If a polymer consists of multiple monomers that form polymeric chains with each other, the material will only have one glass transition temperature. However, if a polymer contains multiple co-monomers, but the monomers prefer to form chains consisting of a singular type of monomer rather than intermingling, then it will have individual thermal glass transition temperatures for each homopolymer (Brazel, 2012). This reveals information on the compatibility of components within a polymer and the homogeneity of the polymerized network.

The 2nd portion is the change in reverse heat flow as a material transitions between a glassy and a rubbery state (Brazel, 2012). As specified earlier, when a polymer transitions from a rigid or glassy state to a rubbery state, a polymer is exposed to enough thermal energy that side groups and portions of main chains become able to overcome secondary forces that once held them in place. This allows the polymer chains to be more mobile and flexible, resulting in a material having more rubbery characteristics. However, this also increases the amount of heat required to raise the temperature of 1 [g] of the polymer by 1[C], also known as the specific heat capacity (Brazel, 2012). This is because enough thermal energy must now be provided to not only raise the overall temperature of the polymer, but to also compensate for the thermal energy
used by the polymer chains to maintain a mobile-like state. However, the mobility and flexibility are limited by the covalent bonds formed during cross linking since the influx of thermal energy during this phase transition is not enough to break the covalent bonds (Brazel, 2012). This limits the mobility of the chains and therefore the amount of heat required to keep them in a semi-mobile state. This allows for the change in reverse heat flow of the polymer during the phase change to indicate the degree of cross linking in the material.

The 3rd and final portion is the temperature range at which the polymer transitions between a glassy and a rubbery state. This is investigated because it reveals the homogeneity of the chemical structure of the polymer [the influence of chemical structure]. Once reaching the thermal glass transition temperature, the polymer obtains enough thermal energy for the movement of small sections of polymer chains, such as side groups or small sections of the main chain. For a homogenous polymer, the amount and types of bonds are uniform, so all the secondary bonds are overwhelmed by thermal energy at or near the same temperature. For heterogenous polymers, bonding within the polymer is not uniform so while certain sections may have a greater density of bonds, which require larger amounts of thermal energy, other sections may contain very little bonding which means less thermal energy is required for chain movement. This results in the transition from a glassy or a rubbery state to occur over a wider range of temperatures. Therefore, by comparing the range of temperatures at which the phase transition between a glassy and rubbery state occurs, it is possible to qualitatively compare the homogeneity of the polymer.

**Thermal degradation**

The 2nd phase investigated is temperature at which the thermal degradation occurs as indicated by 5% mass lose in the polymer (Brazel, 2012). The point of thermal degradation
marks the temperature at which main chain scission occurs which causes an irreversible, structural damage to a polymer and allows for the release of these broken components into the surrounding environment. Therefore, it is important to know the polymer in question is not exposed to an environment at which thermal degradation occurs, whether during fabrication, storage, or general usage.

**Key Aqueous Based Properties**

**Water Miscibility**

Water miscibility, other the ability to fully dissolve in water, is important for polymers that must function in a hydrophilic environment and that must adhere to wet substrates. Differences in the electronegativity of atoms bound together causes an unequal sharing of electrons between the two atoms, resulting in one of the atoms possessing more of the electrons, giving the atom a partial negative charge, while the other atom possess less, giving the atom a partial positive charge (Kotz, 2012). These polar molecules, such as water, tend to attract each other due to the dipole-dipole interaction between the electron rich portions of a polar molecule with the electron poor portions of other polar molecules, causing the formation of hydrogen bonds (Kotz, 2012). However, this gives polar molecules a preference for other polar molecules to the point they tend to avoid interacting with non-polar molecules. The preferential treatment is expressed to a higher degree at the surface of polar fluids due to the polar molecules at the surface of a fluid having less polar molecules to interact with compared to more internally placed molecules, causing the surface molecules to have an even higher attraction toward each other to the point that surface tension is created (Burdon, 2014). Unless enough surface energy is provided to overcome this cohesion of the surface molecules, fluids with differing polarities will express phase separation rather than miscibility and surfaces and fluids with differing polarities will have lower wettability, causing the fluid to bunch up on a surface in droplet form rather than
spreading over a surface (Kotz, 2012) (Aliofkhazraei, 2015). The ease of absorption and wettability have a major impact on the ability of a polymer to form a connection with a desired surface therefore the hydrophilic nature of many environments, such as hydrated dentin in teeth, gives great importance to water miscibility with hydrophilic polymers (Pizzi, 2017) (Nishitani, 2006).

**Solubility**

A useful parameter for any polymer is solubility. While crosslinking generally impedes solvent infiltrating and dissolving the polymer, solvents may infiltrate loosely cross-linked or hydrophilic domains. A hydrophilic domain that exhibits limited monomer-to-polymer conversion may be particularly vulnerable to solvent ingress and hydrolytic degradation. As an example, on prolonged exposure to oral fluids, water penetrates the loosely cross-linked or hydrophilic domains of methacrylate-based dental adhesives. The presence of water promotes the chemical hydrolysis of ester bonds in methacrylate materials. This reaction may be relatively slow at the neutral pH typical of saliva, but excursions in pH caused by foods, beverages, or cariogenic bacteria may lead to transient acid or base catalysis. The carboxylate and alcohol degradation products of ester hydrolysis are more hydrophilic than the parent ester, further enhancing the local ingress of water. This example illustrates the importance and relevance of solubility in assessing the performance of hydrophilic polymers.

**Water Sorption**

Water sorption is another useful parameter. Water sorption refers to the amount of water adsorbed and absorbed by a polymer as the polymer swells. Water can cause plasticization which will change the structural, thermal, and mechanical properties of the polymer. However, swelling may be limited based on the hydrophilicity and cross-linking density of the polymer. This means that water sorption results can reveal information relevant to polymer structure analysis.
Swelling Equilibrium and Rate

Key properties for a hydrophilic polymer are the time required to reach maximum swelling and the final swelling equilibrium value. As mentioned in previous sections, water-induced swelling can impact the structural, thermal, chemical, and mechanical properties of a hydrophilic polymer. One of these changes is the increase in volume as the polymer network swells to accommodate the water. While the volume increase may counteract the stress caused by polymerization shrinkage, too much swelling may have a detrimental impact on properties and performance of the hydrophilic polymer. The rate of swelling may also impact the properties and performance of the hydrophilic polymer. These relationships highlight the importance of determining both the swelling equilibrium value and the time required to reach this value.

Density

Another important parameter that can be obtained from the swelling equilibrium experiment is density. The overall density of a material provides a relationship between the mass and the volume of a material and can be used to determine the various ratios of components within a formulation. Density is also a common variable utilized in many equations such as the Flory-Rehner equation.

Gel Fraction

During the polymerization process it is not uncommon for some components to remain unpolymerized. Crosslinking that occurs as the polymer polymerizes will lead to decreased chain mobility due to a decrease in available free volume and an increase in secondary forces and entanglement. This can cause unpolymerized monomer and/or oligomer to be trapped within the cured polymer. Environmental factors such as thermal energy or solvent-provoked plasticization may increase mobility of the polymer chains and the trapped monomer or oligomer.
This delayed mobility can alter the polymer network. The now mobile unpolymerized species may react with the polymer network, react with other species within the network that are not fully polymerized, or it may be leached from the network — the result of these reactions will be a change in the initial properties. For example, leaching may lead to voids that can be infiltrated by solvent — this could lead to plasticization and deterioration of the properties. Monomer that leaches from the polymer may interact with the local environment and this activity could lead to environmental or biological damage — the nature of the damage will depend on the application. Leached species could also interact with the local environment to cause damage to the polymer network or the surrounding tissues when the polymer is used in various biomedical applications.

Studying how the gel fraction changes over time can reveal how long it takes for a solvent to fully penetrate a cured structure or the time it takes for specific components to leach. Understanding the gel fraction of a polymer can allow investigators to use the leaching process to design and develop biodegradable gels for the delivery of medication, e.g., investigators use their understanding of the leaching process to produce gels that will deliver medication at specific rates and locations. Investigators also use their understanding of the leaching process to develop hydrogels that are tailored for specific biomedical applications including tissue-engineering constructs. These examples highlight the importance of studying the gel fraction, or the mass fraction of cured material within the polymer by monitoring not just the unreacted species, but the rates at which these species are leached from the hydrophilic polymer.
Key Rheological Based Properties

Phase Angle

A key property at the core of any rheological testing is the phase angle (d). The phase angle is a value ranging from 0 to 90 [deg] which provides a quantifiable way of representing where on the viscoelastic spectrum a material lies. The range of 0 to 90 [deg] originates from how elastic materials have an instantaneous relationship between stress and strain while viscous materials have a time dependent relationship between stress and strain (Brazel, 2012). This is shown in the equations below representing a scenario where a frequency-based, sinusoidal shear strain is applied to a purely elastic and purely viscous material and measuring the sinusoidal, shear stress in response.

\[ \gamma(t) = \gamma_0 \sin(wt) \]

Where “w” is the angular frequency [radians/sec]

For Purely Elastic Materials (d = 0 [rad] or 0 [deg])

\[ \tau = G \gamma(t) \]

\[ \tau = G \gamma_0 \sin(wt + 0) \]

For Purely Viscous Materials (d = \pi/2 [rad] or 90 [deg])

\[ \tau = n \dot{\gamma} = \frac{n \gamma}{dt} \cdot \frac{\tau}{n} dt = \gamma \& \sin \left(x + \frac{\pi}{2}\right) = \cos(x) \]

\[ \frac{\tau}{n} dt = \gamma_0 \sin(wt) \]

\[ \tau = \frac{n \gamma_0 \sin(wt)}{dt} = n \gamma_0 \cos(wt) \cdot w = n \gamma_0 w \sin\left(wt + \frac{\pi}{2}\right) \]

As shown by the scenario for a purely elastic material, the resulting phase angle between the shear strain and shear stress is 0 [rad] or 0 [deg] due to the instantaneous responsive nature of purely elastic materials while the resulting phase angle from the purely viscous material scenario is \pi/2 [rad] or 90 [deg] due to the time dependency between the shear stress and strain.

Viscoelastic materials, which possess both elastic and viscous properties, will therefore produce
a phase angle between 0 and 90 [deg]. This allows one to identify whether a material possesses more elastic or viscous properties based on the phase angles proximity to 0 and 90 [deg] respectively and can be used to monitor how a viscoelastic material changes in response to external factors. The phase angle is used to separate the complex modulus, which represents how the elastic and viscous portions of a material act as a whole in response to stress or strain, into two distinct variables: the storage modulus (\(G'\)), which represents the elastic properties, and the loss modulus (\(G''\)), which represents the viscous properties.

\[
G^* = \frac{\tau_0}{\gamma_0}; \tan(d) = \frac{G''}{G'}
\]

*Figure 1: Relationship between Complex, Storage, and Loss Moduli and Phase Angle*

*Equation 11: Complex Modulus and Phase Angle Equations*
Storage Modulus: $G'$

The storage modulus, named after the ability of a viscoelastic material to store energy from applied stress or strain, is also known as the in-phase moduli and the elastic moduli (Brazel, 2012) (Dawn, 2017). Materials with higher storage modulus values possess greater elastic-based properties such as a more instantaneous response to applied forces, a more solid-like structure, and a higher degree of stiffness (Brazel, 2012). The storage modulus is also used to represent the structural integrity of a material and is used in many experiments to determine factors such as yielding when under various loads, frequencies, and environmental factors and phase changes such as during a curing process. The storage modulus is calculated using the equation below:

$$G' = \frac{\tau_0}{\gamma_0} \cos(d)$$

*Equation 12: Storage Modulus Equations*

Loss Modulus: $G''$

The second modulus is the Loss modulus, also known as the out-of-phase modulus and the viscous modulus (Brazel, 2012). The loss modulus reveals how viscous materials dissipate, or lose, energy in the form of heat rather than elastically responding to the applied forces (Brazel, 2012). Materials with high loss moduli tend to possess more liquid-like characteristics, dampen applied forces, and deform easily (Brazel, 2012). The loss modulus can also be used to determine changes in chain mobility within a structure. The loss modulus is calculated using the equation below:

$$G'' = \frac{\tau_0}{\gamma_0} \sin (d)$$

*Equation 13: Loss Modulus Equation*

Viscosity

Viscosity represents the ability of a liquid to resist flow and originates from the relationship between shear stress and shear rate in viscous materials (Brazel, 2012). As a fluid
flows, the mass that makes up the body of fluid is constantly experiencing positional displacement in the direction of its flow velocity gradient as can be seen from Figure 2 below which represents a 1-dimensional, laminar flow of a fluid.

![Figure 2: 1-Dimensional, Laminar Fluid Flow with Shear](image)

When the fluid flows across a surface, a frictional shear force is created which acts in the opposing direction of the net fluid flow. Although this reduces the displacement of the fluid’s mass, the impact of the frictional force decreases with distance from the surface creating a relationship between the change in position of the mass of water with the change in the distance between the mass and the surface creating the shear force. This relationship is named “shear strain”. When the derivative of shear strain is taken with respect to time, the equation transforms to represent the relationship between the fluid velocity and distance between the fluid and the surface applying the shear force which is known as shear (strain) rate. Therefore, as the amount of shear stress applied changes on a fluid, so does the resulting shear rate as shown in Equation 10: Newton’s Law of Viscosity.

This relationship between viscosity, shear stress, and shear rate is highly useful when investigating a polymer because if two of the values are known the third can be easily found. In many industrial settings, such as a chemical or food processing plant, industrial rated equipment may be used to mix large batches of product or move liquids through pipe systems. The viscosity
of the product can then be used to determine if an industrial mixer can apply enough shear forces to mix the product without permanently damaging a motor or to ensure that components are flowing at the correct rates so that the final product has the correct composition. Viscosity values of medical products, such as vaccines, medications, or blood transfusions, ensure that the product can enter the patient through an IV or needle at a specific shear rate without creating enough shear stress to permanently damage the molecular structure of medication or cell membranes before entering the patient.

For many simplistic fluid-like materials such as gases, water, or some solvents such as toluene, the small, relatively symmetrical molecules do not alter the overall molecular structures and orientations within the material as the amount of applied shear stress or shear rate changes. These materials are labeled as “Newtonian” since they follow Newtons law of viscosity, as shown below, which depicts a linear relationship between shear stress and shear rate. However, most viscoelastic materials do not follow this principle. These materials can be created from a wide variety of combinations of polymer chains with differing molecular structures in order to obtain specific bonding or molecular orientations to best fit a specific application. Unlike the smaller, symmetrical molecules in Newtonian fluids, longer polymer chains introduce factors such as chain entanglement and bonding which can rapidly change the overall molecular orientation, and therefore viscosity, of the material once sufficient values of shear stress or shear rate are obtained or lost. These “Non-Newtonian” fluids can express non-linear relationships between shear stress and shear rate such as dilatant (shear-thickening) or pseudoplastic (shear-thinning) characteristics. Some non-Newtonian fluids are also time-dependent, showing rheopectic (increasing viscosity) or thixotropic (decreasing viscosity) when exposed to constant shear stress or shear rate over time while able to return to their original viscosity values when the
applied forces are removed. Some materials contain a combination of Newtonian and non-Newtonian characteristics depending on the amount of applied shear stress or shear rate to the material. In general, when viewing polymer melts and solutions over several decades of shear stress or shear rate, the overall viscosity values can be broken down into 3 phases. At low shear rates or stresses, the polymers express Newtonian characteristics and a constant viscosity value labeled as the zero-shear viscosity due to how chain entanglement and secondary bonding allows the polymers to resist any changes to their molecular orientation. Eventually, the applied shear stress or rate ramps to a point that the polymer chains begin to untangle and align themselves with the applied shear stress or rate causing the material to express pseudoplastic (shear thinning) characteristics. Once reaching severe shear stresses or rates, the polymers reach the third phase known as the “upper Newtonian phase”. In this phase the polymer chains have untangled and aligned themselves with the direction of the applied shear stress or rate, causing the material to once again express Newtonian characteristic.

It is very important with any polymer to investigate the viscosity under multiple decades of shear stress or shear rate because only testing the viscosity of a polymer under a short range of values can lead to inaccurate characterization of the material. For example, if a researcher that is designing a new polymer only tests viscosity values under a single decade of high shear rate values, which happened to be in the polymer’s upper Newtonian phase, the investigator may incorrectly conclude that the polymer shows only Newtonian characteristics and therefore allows for Newton’s law to be applied at any desired shear stress or shear rate value. In reality, the polymer may show phases of pseudoplasticity or a higher zero-shear viscosity at lower shear rates, as discussed above with polymer melts and solutions. Not only does this result in non-reproducible data but can lead to incorrectly designed manufacturing methods or the inability to
function properly which depending on the application can cause the loss of time, money, and lives.

Results

Averages and Standard Deviations

Degree of Conversion Averages and Standard Deviations

<table>
<thead>
<tr>
<th>Hydrophilic Polymer</th>
<th>Average [%]</th>
<th>SD [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>73.83</td>
<td>1.33</td>
</tr>
<tr>
<td>E2.5</td>
<td>76.03</td>
<td>0.434</td>
</tr>
<tr>
<td>E5.0</td>
<td>75.17</td>
<td>0.108</td>
</tr>
<tr>
<td>E7.5</td>
<td>75.04</td>
<td>1.36</td>
</tr>
<tr>
<td>E10</td>
<td>68.37</td>
<td>1.24</td>
</tr>
</tbody>
</table>

*Table 4: Averages and SDs for Degree of Conversion*

As seen from Table 4, the highest average DoC belongs to e2.5 followed by e5.0, e7.5, co, then e10. Hydrophilic polymers co, e2.5, e5.0, and e7.5 all present average DoC within a 2.2 [%] range, but e10 presents a much lower DoC at 68.37 which is 5.46[%] lower than the next lowest DoC belonging to co.

Thermal Degradation Averages and Standard Deviations

<table>
<thead>
<tr>
<th>Hydrophilic Polymer</th>
<th>Average</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>280.21</td>
<td>10.24</td>
</tr>
<tr>
<td>E2.5</td>
<td>270.95</td>
<td>41.98</td>
</tr>
<tr>
<td>E5.0</td>
<td>277.15</td>
<td>40.93</td>
</tr>
<tr>
<td>E7.5</td>
<td>274.02</td>
<td>10.39</td>
</tr>
</tbody>
</table>
As seen by Table 5, hydrophilic polymer co showed the highest average temperature at which 5% of mass loss occurred followed by e5.0, e10, e7.5, and finally e2.5. The averages exist over a range of 9.26 [C] and produce an overall average temperature at which 5% of the mass of a sample is lost at of 275.89 [C]. These values reveal no obvious pattern between weight percentage of MPS or TEGDMA and temperature at which 5% of mass was lost.

**Table 5: Averages and SDs for Thermal Degradation**

<table>
<thead>
<tr>
<th>Hydrophilic Polymer</th>
<th>Average [C]</th>
<th>SD[C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>118.76</td>
<td>1.37</td>
</tr>
<tr>
<td>E2.5</td>
<td>117.31</td>
<td>4.03</td>
</tr>
<tr>
<td>E5.0</td>
<td>115.95</td>
<td>4.97</td>
</tr>
<tr>
<td>E7.5</td>
<td>111.39</td>
<td>2.18</td>
</tr>
<tr>
<td>E10</td>
<td>113.85</td>
<td>2.82</td>
</tr>
</tbody>
</table>

**Table 6: Averages and SDs for Thermal Glass Transition Temperature**

<table>
<thead>
<tr>
<th>Hydrophilic Polymer</th>
<th>Average [W/g]</th>
<th>SD[W/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>5.03e-3</td>
<td>2.32e-3</td>
</tr>
<tr>
<td>E2.5</td>
<td>6.23e-3</td>
<td>3.27e-3</td>
</tr>
<tr>
<td>E5.0</td>
<td>3.67e-3</td>
<td>1.83e-3</td>
</tr>
<tr>
<td>E7.5</td>
<td>3.47e-3</td>
<td>2.87e-3</td>
</tr>
<tr>
<td>E10</td>
<td>4.30e-3</td>
<td>2.16e-3</td>
</tr>
</tbody>
</table>

**Table 7: Averages and SDs for Signal Change**
The Temperature Range for each Hydrophilic Polymer [C]

<table>
<thead>
<tr>
<th>Hydrophilic Polymer</th>
<th>Average [C]</th>
<th>SD[C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>18.05</td>
<td>2.29</td>
</tr>
<tr>
<td>E2.5</td>
<td>27.01</td>
<td>8.60</td>
</tr>
<tr>
<td>E5.0</td>
<td>19.22</td>
<td>9.56</td>
</tr>
<tr>
<td>E7.5</td>
<td>19.89</td>
<td>14.08</td>
</tr>
<tr>
<td>E10</td>
<td>19.16</td>
<td>6.08</td>
</tr>
</tbody>
</table>

Table 8: Averages and SDs for Temperature Change

Thermal Glass Transition Temperature:
As seen from Table 6, the Tg is highest for co followed by e2.5, e5.0, e10, and e7.5. A pattern appears from the table where the data forms almost 2 plateaus: 1 consisting of co and e2.5 and the other consisting of e7.5 and e10 while e5.0 acts almost as a transition point between the two plateaus. The overall average thermal glass transition temperature for the entire data set is 115.45±2.91 [C] and the averages cover a range of 7.37 [C].

Signal Change:
As seen from Table 7, the signal change is highest for e2.5 then co, e10, e5.0, and finally e7.5. Although all of the signal change values are relatively small, the overall average change in specific heat capacity for the hydrophilic polymers is 4.54e-3±1.13e-3 [W/g].

Temperature Range:
As seen from Table 8, the range of temperature the phase transition occurs over is largest for e2.5 then e7.5, e5.0, e10, and finally co. All of the hydrophilic polymers except e2.5 have average ranges of temperature within a range of 1.84 [C]. However, e2.5 is not only the largest, but is 7.12 [C] larger than the next highest average value. The overall average temperature range is 20.67±3.608 [C] and all of the average temperature range values exist across a range of 8.96 [C]. Compared to co which contains no MPS, the 4 other hydrophilic polymers have much
higher variances as seen by how the standard deviation is ± 2.29 [C] for co and e2.5, e5.0, e7.5, and e10 possess standard deviations of ± 8.60, ±9.56, ±14.08, and ±6.08 [C].

**Water Miscibility Averages and Standard Deviations**

<table>
<thead>
<tr>
<th>Hydrophilic Polymers</th>
<th>Average [%]</th>
<th>SD [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>62.26</td>
<td>0.61</td>
</tr>
<tr>
<td>E2.5</td>
<td>55.57</td>
<td>1.18</td>
</tr>
<tr>
<td>E5.0</td>
<td>51.60</td>
<td>0.30</td>
</tr>
<tr>
<td>E7.5</td>
<td>46.87</td>
<td>0.62</td>
</tr>
<tr>
<td>E10</td>
<td>44.04</td>
<td>1.32</td>
</tr>
</tbody>
</table>

*Table 9: Averages and SDs for Water Miscibility*

As seen in Table 9, the average weight percentage of DIH$_2$O required for water miscibility of the hydrophilic polymer decreased as the weight percentage of TEGDMA decreased and MPS increased with the largest weight percentage of DIH$_2$O required for water miscibility expressed by co then e2.5, e5.0, e7.5, and finally e10.

**Solubility and Sorption Averages and Standard Deviations**

**Solubility**

<table>
<thead>
<tr>
<th>Hydrophilic Polymer</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>6.57</td>
<td>7.17</td>
</tr>
<tr>
<td>E2.5</td>
<td>2.94</td>
<td>3.54</td>
</tr>
<tr>
<td>E5.0</td>
<td>1.43</td>
<td>1.26</td>
</tr>
<tr>
<td>E7.5</td>
<td>3.85</td>
<td>3.35</td>
</tr>
<tr>
<td>E10</td>
<td>2.26</td>
<td>1.02</td>
</tr>
</tbody>
</table>

*Table 10: Averages and SDs for Original Solubility Values*
### Log10 Transformed Solubility [%]

<table>
<thead>
<tr>
<th>Hydrophilic Polymer</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>0.59</td>
<td>0.50</td>
</tr>
<tr>
<td>E2.5</td>
<td>0.30</td>
<td>0.39</td>
</tr>
<tr>
<td>E5.0</td>
<td>0.39</td>
<td>0.24</td>
</tr>
<tr>
<td>E7.5</td>
<td>0.56</td>
<td>0.30</td>
</tr>
<tr>
<td>E10</td>
<td>0.31</td>
<td>0.21</td>
</tr>
</tbody>
</table>

*Table 11: Averages and SDs for Log Transformed Solubility Values*

As seen in Table 10, the original or untransformed values for the solubility values for the hydrophilic polymers are 6.57±7.17 [%] for co, 2.94±3.54 [%] for e2.5, 1.43±1.26 [%] for e5.0, 3.85±3.35 [%] for e7.5, and 2.26±1.02 [%] for e10. This reveals a general trend of the average solubility values for e2.5, e5.0, e7.5, and e10 covering a range of 2.42 [%] however, co has a much higher average solubility which is 2.72 [%] higher than the 2nd highest average solubility value.

After failing the normality of distribution testing, the dataset was transformed via a log transformation, changing the averages and standard deviations into the values shown in Table 11: Averages and SDs for Log Transformed Solubility Values

of 0.59±0.50 [%], 0.30±0.39 [%], 0.39±0.24 [%], 0.56±0.30 [%], and 0.31±0.21 [%] were reported for co, e2.5, e5.0, e7.5, and e10 respectively.

### Water Sorption [%]

<table>
<thead>
<tr>
<th>Hydrophilic Polymer</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>63.92</td>
<td>5.23</td>
</tr>
</tbody>
</table>

*Water Sorption*
Table 12: Averages and SDs for Water Sorption

The water sorption percent values for co, e2.5, e5.0, e7.5, and e10 are 63.92±5.23 [%], 72.65±2.90 [%], 77.86±0.78 [%], 81.28±2.84 [%], and 91.50±2.32 [%] as shown in Table 12. These values reveal an obvious trend of the percent water sorption values increasing as the weight percentage of MPS increased and the weight percentage of TEGDMA decreased.

Swelling Ratio and Density Averages and Standard Deviations

Density

<table>
<thead>
<tr>
<th>Hydrophilic Polymer</th>
<th>Avg</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>1.28</td>
<td>0.03</td>
</tr>
<tr>
<td>e2.5</td>
<td>1.27</td>
<td>0.01</td>
</tr>
<tr>
<td>e5.0</td>
<td>1.28</td>
<td>0.01</td>
</tr>
<tr>
<td>e7.5</td>
<td>1.27</td>
<td>0.02</td>
</tr>
<tr>
<td>e10</td>
<td>1.28</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 13: Averages and SDs for Density

As seen from Table 13, all of the hydrophilic polymers are similar in value with 1.28±0.03 [g/cm3] for co, 1.27±0.01 [g/cm3] for e2.5, 1.28±0.01 [g/cm3] for e5.0, 1.27±0.02 [g/cm3] for e7.5, and 1.28±0.01 [g/cm3] for e10.

Swelling Ratio
As seen from Table 14, the average swelling ratio values for all hydrophilic polymers increase dramatically within the first 10 hours of soaking in DIH$_2$O, but then tend to stabilize. This is seen by how within the first 10 hours the swelling ratios change by 85.23±6.90, 94.18±4.77, 93.31±3.37, 100.92±6.93, and 106.44±5.20 [%], but by 72 hours the swelling ratios are 84.37±8.42, 94.86±5.83, 94.95±1.51, 101.00±5.89, and 108.09±3.66 [%] for co, e2.5, e5.0, e7.5, and e10 respectively. The average values also show a pattern where the swelling ratio increases as the weight percentage of MPS increases and TEGDMA decreases as seen by the values for hours 1, 3, 24, and 72. For hours 5, 10, and 48, the only change in the previous pattern is that e2.5 expresses higher values than e5.0.

<table>
<thead>
<tr>
<th>Hydrophili c Polymer</th>
<th>hour 0</th>
<th>hour 1</th>
<th>hour 3</th>
<th>hour 5</th>
<th>hour 10</th>
<th>hour 24</th>
<th>hour 48</th>
<th>hour 72</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Avg</td>
<td>0.00</td>
<td>34.44</td>
<td>59.75</td>
<td>74.13</td>
<td>85.23</td>
<td>82.86</td>
<td>84.51</td>
</tr>
<tr>
<td></td>
<td>Sd</td>
<td>0.00</td>
<td>7.32</td>
<td>6.38</td>
<td>7.61</td>
<td>6.90</td>
<td>8.65</td>
<td>6.32</td>
</tr>
<tr>
<td>e2.5</td>
<td>Avg</td>
<td>0.00</td>
<td>39.27</td>
<td>64.68</td>
<td>83.60</td>
<td>94.18</td>
<td>92.90</td>
<td>94.59</td>
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<tr>
<td></td>
<td>Sd</td>
<td>0.00</td>
<td>1.57</td>
<td>1.18</td>
<td>3.06</td>
<td>4.77</td>
<td>2.36</td>
<td>3.73</td>
</tr>
<tr>
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<td>Avg</td>
<td>0.00</td>
<td>41.25</td>
<td>65.15</td>
<td>82.05</td>
<td>93.31</td>
<td>95.60</td>
<td>94.31</td>
</tr>
<tr>
<td></td>
<td>Sd</td>
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<td>3.65</td>
<td>2.17</td>
<td>2.22</td>
<td>3.37</td>
<td>2.63</td>
<td>1.92</td>
</tr>
<tr>
<td>e7.5</td>
<td>Avg</td>
<td>0.00</td>
<td>46.50</td>
<td>72.73</td>
<td>87.92</td>
<td>100.92</td>
<td>100.28</td>
<td>100.55</td>
</tr>
<tr>
<td></td>
<td>Sd</td>
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<td>1.78</td>
<td>1.84</td>
<td>3.54</td>
<td>6.93</td>
<td>4.60</td>
<td>3.18</td>
</tr>
<tr>
<td>e10</td>
<td>Avg</td>
<td>0.00</td>
<td>50.07</td>
<td>80.72</td>
<td>96.39</td>
<td>106.44</td>
<td>108.38</td>
<td>108.50</td>
</tr>
<tr>
<td></td>
<td>Sd</td>
<td>0.00</td>
<td>3.87</td>
<td>7.45</td>
<td>4.83</td>
<td>5.20</td>
<td>4.38</td>
<td>4.95</td>
</tr>
</tbody>
</table>

Table 14: Averages and SDs for Swelling Ratio

Gel Fraction Averages and Standard Deviations

44
### Averages and Standard Deviations for Gel Fraction [mg/mg]

<table>
<thead>
<tr>
<th>Hydrophilic Polymer</th>
<th>day 1</th>
<th>day 2</th>
<th>day 3</th>
<th>day 4</th>
<th>day 5</th>
<th>day 6</th>
<th>day 7</th>
<th>day 20</th>
<th>day 22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Avg</td>
<td>1.00</td>
<td>1.37</td>
<td>1.06</td>
<td>1.03</td>
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<td>1.01</td>
<td>1.01</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>Sd</td>
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<td>0.04</td>
<td>0.04</td>
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<td>Avg</td>
<td>1.00</td>
<td>1.41</td>
<td>1.10</td>
<td>1.07</td>
<td>1.06</td>
<td>1.05</td>
<td>1.05</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>Sd</td>
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<td>0.02</td>
<td>0.01</td>
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<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>e5.0</td>
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<td>1.42</td>
<td>1.09</td>
<td>1.06</td>
<td>1.05</td>
<td>1.04</td>
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<tr>
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<td>0.03</td>
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<td>0.03</td>
<td>0.03</td>
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<tr>
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<td>1.43</td>
<td>1.08</td>
<td>1.06</td>
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<td>0.04</td>
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</tr>
<tr>
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<td>Avg</td>
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<td>1.41</td>
<td>1.08</td>
<td>1.05</td>
<td>1.04</td>
<td>1.03</td>
<td>1.03</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>Sd</td>
<td>0.00</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

#### Table 15: Averages and SDs for Gel Fraction (Gel Fraction Form)

As seen in Table 15, all hydrophilic polymers acted in a similar manner. The gel fraction values were highest for day 0 and then dropped rapidly by day 1 after which only small changes in the gel fraction value occurred. Although co’s gel fraction dropped below 1 by day 6, the 4 other experimental, hydrophilic polymers all possessed average gel fraction values above 1 even after 22 days of drying.

### Statistical Analysis Information

#### Required Assumptions

**Normality Assumption: Shapiro-Wilk Test**

To test if a data set was normality distributed the Shapiro-Wilk (SW) Test was chosen.

The Shapiro-Wilk test was chosen because the test has been shown to be more powerful compared to other normality tests such as the Anderson-Darling, Lilliefors, and Kolmogorov-
Smirnov test which will help counteract the loss in power due to small samples sizes used in various experiments (Razali, 2012).

The SW test functions as follows. First the Shapiro-Wilk statistic (W) is produced by running the population through the equation

\[
W = \frac{\sum_{i=1}^{m} a_i (x_{n+1-i} - x_i)^2}{\sum_{i=1}^{n} (x_i - \bar{x})^2}
\]

*Equation 14: Shapiro-Wilk W Statistic Equation*

Where \( x \) are the sample values of the population, \( n \) is the number of samples in a population, and \( a \) are weights obtained from Shapiro-Wilk Tables based on the value of \( n \) (Zaiontz, 2020). The variable \( m \) is equal to \( (n/2) \) if \( n \) is an even number and \((n-1)/2\) if \( n \) is an odd number (Zaiontz, 2020). \( W \) is used with 2 pairs of \( p \)-values and \( W \) values obtained from the Shapiro-Wilk Tables to determine the \( p \)-value for the population through linear interpolation. If the produced \( p \)-value for the population is greater than the arbitrary alpha value, this shows there is not sufficient statistically significant evidence to reject the null hypothesis (Ho) shown below and that the samples come from a population with normally distributed means. However, if the \( p \)-value for the population is lower or equal to the arbitrary alpha in value than there is statistically significant evidence that the samples do not come from a population with normally distributed means and instead follow the alternative hypothesis (Ha) shown below.

\[
H_o = \text{The samples come from a population with a normal distribution of means}
\]

\[
H_a = \text{The samples do not come from a population with a normal distribution of means}
\]

If sample sizes are larger than 30, the population can be assumed to be normal since according to the central limit theory large samples (>30) tend to be normal regardless of the shape of the data (Ghasemi, 2012).
For this thesis, the “Shapiro-Wilk Test Calculator” from Statistics Kingdom was used for normality testing of populations (Shapiro-Wilk Test Calculator, 2017).

**Homogeneity of Variance: The Brown-Forsythe Test**

In order to determine if a dataset expresses homogeneity in variance, the Brown-Forsythe (BF) Test was used. The BF test is a modification of the Levene test that uses medians rather than means in its calculations (Glen, 2015). This helps correct for skewness in the population which makes the BF test more robust and less likely than the Levene test to show the homogeneity of variance assumption has been violated incorrectly (Wang, 2017). The test is very straight forward with the median value for each group of the population being subtracted from all of the samples in each group then the absolute value is taken for each difference so that all difference values are positive as shown below.

\[
    x_{i,j,\text{modified}} = \text{abs}(x_{i,j,\text{original}} - \text{median}_{j,\text{original}})
\]

*Equation 15: Brown-Forsythe Equation*

Where “I” equals 1 through n samples and “j” equals 1 through k groups

The modification to the groups makes it so that the only difference between groups in the population is each groups variability. The population, now with modified groups, is then run through an ANOVA test to obtain a p-value. If the p-value is less than the arbitrary alpha in value, there is enough statistically significant evidence to reject the null hypothesis that all groups in the population express homogeneity of variance and instead the alternative hypothesis (Ha) is assumed which states that at least one group expresses a variance different than the other groups as shown below. If the p-value is equal or above the assumed alpha, there is not sufficient evidence to reject the null hypothesis that all groups in the population express homogeneity of variance.
\[ H_0 = \text{All groups within a population express homogeneity of variance} \]

\[ H_a = \text{At least one group within a population has a variance not equal to the other groups} \]

**Sphericity: Greenhouse-Geisser and Huynh-Feldt Correction Factors**

For repeated measures-based testing, one must not just account for variance within treatments, but also the covariance between treatments (Field, 1998). This is done by proving the population fulfills the sphericity assumption that there is equality of variances for the differences between all treatment levels (Field, 1998). A population that does not fulfill the sphericity assumption can have an increased chance of type 1 errors, but correction factors such as the Greenhouse-Geisser (GG) correction and the Huynh-Feldt (HF) correction can be applied to the degrees of freedom to correct this violation as shown below (Abdi, 2010).

**GG: correction**

\[
GG: \text{correction} = \frac{(\sum_a s_{a,a})^2}{(A - 1) \sum_{a,a'} s_{a,a'}^2}
\]

*Equation 16: Greenhouse-Geisser Correction Factor Equation*

\[ s_{a,a'} = (t_{a,a'} - \bar{\epsilon}) - (t_a - \bar{\epsilon}) - (t_{a'} - \bar{\epsilon}) = t_{a,a'} - t_a - t_{a'} + \bar{\epsilon}
\]

Where \( t_{a,a'} \) = the sample estimate of the covariance between the groups \( a \) and \( a' \), \( t_a \) = mean of the covariances for group \( a \), \( t_{a'} \) = mean of covariances for group \( a' \), and \( \bar{\epsilon} \) = grand mean of the covariance table

**HF: correction**

\[
HF: \text{correction} = \frac{S(A - 1) \epsilon_i - 2}{(A - 1)(S - 1 - (A - 1)\epsilon_i)}
\]

*Equation 17: Huynh-Feldt Correction Factor Equation*

Where \( A \) = treatment levels, \( S \) = population size, \( \epsilon_i \) = epsilon value, \( s_{a,a'} \) = the sample estimate of the covariance between groups \( a \) and \( a' \), \( s_{a,a} \) = the variance within treatment \( a \)

Which correction is chosen depends on the epsilon value for the Greenhouse-Geisser correction factor. Due to the overly conservative nature of the GG correction and the liberal nature of the HF correction, deciding which correction value goes as follows (Abdi, 2010):
1) If the GG correction value is 1 or close to 1, the population can be assumed to fulfill the sphericity assumption and the correction is not needed
2) If GG correction value is 0.75 or larger without being close to 1, the GG correction should be used
3) If the GG correction value is below 0.75, the HF correction should be used

The sphericity assumption is automatically assumed to be fulfilled for populations with only 2 levels of treatment, such as in pair wise comparisons. This is because when there are only 2 treatment levels, only 1 covariance between treatments is possible. Therefore, there is no other covariance between treatments to be compared to making it impossible to fail the sphericity assumption.

**Point Effect Size with 95% Confidence Interval**

**Why Utilize Both Point Effect Sizes and 95% Confidence Intervals**

The combination of point effect sizes with 95% confidence intervals will be used in the statistical analysis of collected data since using both methods will strengthen the overall analysis of collected data.

When investigating the differences in data populations, it can be difficult to determine whether the differences in populations is significant. Methods such as 95% confidence intervals and a p-values generated from statistical tests, such as a Tukey-Kramer pair-wise comparison, utilize the averages, standard deviations, and samples sizes of populations to determine if there is enough evidence to indicate statistically significant differences between the populations. However, statistical significance alone may not provide a complete picture of the differences between populations. Factors such as excessive sample usage can make even small differences appear to show statistically significance while larger differences can be masked by large standard deviations or small sample usage. This means that while certainty can be investigated, the magnitude of the differences may be overlooked.
Effect sizes provide a way to investigate the magnitude of the differences between populations. Similar to Z-scores, effect sizes represent how the average sample of one population is greater or lower than a specific percent of another population giving an indication of the magnitude of the differences between populations. While sometimes samples sizes are utilized to account for small populations used during testing, effect sizes are mainly influenced by average and standard deviation values which prevents the magnitude of the differences being heavily swayed by excessive or inadequate population sizes. However, the effect sizes generated between populations may only represent the magnitude of the differences between the specific populations used in testing rather than all possible samples for each population in existence. Unlike the true effect sizes between populations, these point effect sizes create a level of uncertainty with their values and therefore lack the ability to show statistically significant differences between populations.

By utilizing point effect sizes and 95% confidence intervals at the same time, the overall statistical analysis of data is greatly improved. Each method covers the other’s weakness allowing for both the magnitude and statistical significance of differences to be investigated. This combination may also reveal information that neither method can provide alone. For example, a chemical factory may discover a new method to make a product. Purely relying on investigating the statistical significance between the product when made with the old and new methods may reveal enough evidence to indicated statistically significant differences between the methods. However, a low point effect size may reveal that although significant, the benefits of transitioning to the new method may not be enough to make up for the loss of resources and capital from modifying the factory and retraining workers. Another possible scenario with the chemical factory is that there is not enough evidence to show a statistically significant difference
between the production methods, but the point size generated by comparing the products of each method may be fairly large. While this may reveal that there is simply no statistically significant benefit to the new method of production, there is also the possibility that flaws in the testing process, such as not using enough samples or using samples with too much variation, can lead to misleading conclusions.

**Effect Sizes: Hedge’s d Point Effect Size**

In order to show that magnitude of the effect or differences between groups, a Hedge’s D effect size will be used. The Hedge’s D effect size was chosen to be used due to its many benefits such as being a standardized mean difference statistical effect size, utilizes a pooled standardized deviation, is corrected for upward bias due to smaller sample sizes, can be used for between and within comparisons, the ability for later meta-analysis, is equivalent to a Z-score, and is relatively simple to calculate (Coe, 2002) (Nakagawa, 2007).

The Hedge’s d is calculated as follows after fulfilling required assumptions for the effect size:

1) A Hedge’s g is calculated

\[ d = \frac{m_2 - m_1}{s_{\text{pooled}}} \]

*Equation 18: Hedge's g Equation*

\[ s_{\text{pooled}} = \sqrt{\frac{(n_2 - 1)s_2^2 + (n_1 - 1)s_1^2}{n_1 + n_2 - 2}} \]

*Equation 19: Pooled SD Equation*

2) The Hedge’s g was corrected for upwards bias into a Hedge’s d

\[ d_{\text{unbiased}} = d_{\text{biased}}[1 - \left(\frac{3}{4(n_1 + n_2 - 2)} - 1\right)] \]

*Equation 20: Hedge's d Equation*
Confidence Interval: 95% Confidence Interval

The 95% confidence interval represents an interval that with 95% confidence contains the true mean population value (Nakagawa, 2007). In other words, if this test was repeated 100 times, each with its own set of samples, 95 of the 100 tests with this confidence interval would contain the true population effect size. It is important to clarify this does not mean there is a 95% chance that the interval contains the true population mean effect size. This is paired with the effect size calculated from the current data set because the Hedge’s d values calculated in this paper are point effect sizes, a type of effect size based off a sample set of the true population, which may or may not be the true population mean effect size (Nakagawa, 2007). This is useful for determining if point effect sizes show that the 2 groups being compared are statistically significantly different because any value within the 95% confidence interval has a chance of being the true mean population effect size so if the interval contains zero, this could be the true mean population effect size. A zero-effect size means that there could be no difference, or no effect, between the standardized means of the two populations being compared and therefore it cannot be claimed there is a statistically significant difference between them.

The 95% confidence interval is calculated with the following equations (Nakagawa, 2007):

\[
95\% \ CI = ES \pm Z_{score} \times se, \text{ where } ES = Effect \ Size, se = asymptotic \ standard \ error
\]

Equation 21: 95% CI Equation

\[
if \ n > 30: Z_{score} = 1.96
\]

\[
if \ n \leq 30: Z_{score} = t_{distribution}(df, \alpha)
\]

If comparison is between treatments (independent) (Nakagawa, 2007):
\[ se_{hedges} = \sqrt{\frac{n_1 + n_2}{n_1 n_2} + \frac{(Hedge's \ d)^2}{2(n_1 + n_2 - 2)}} \]

*Equation 22: Standard Error Equation (Between)*

If comparison is within a treatment, or repeated measures of the same samples (dependent) (Pfister, 2013) (Franz, 1994) (Loftus, 1994):

\[ se_{hedges} = \sqrt{\frac{\sum_i^n (d_i - \bar{d})^2}{n(n - 1)}} \]

*Equation 23: Standard Error Equation (Within)*

Where \( n = \) number of sample comparisons, \( d = \) sample difference.

**Presentation of Results**

The results of the statistical analysis will be presented in a way to the reader so that the results and data are transparent and easily interpretable. The point effect size and 95% confidence interval generated through each comparison of data set populations will be presented in shorthand in the following way:

*point effect size [ 95% Confidence Interval Upper Limit, 95% Confidence Interval Lower Limit, Percentage of Population A (starting from Bottom that the average (50%) value of population B is greater than]*

For this thesis, when comparisons are made between hydrophilic polymers (i.e. an experimental, hydrophilic polymer (e2.5, e5.0, e7.5, or e10) is compared to the control hydrophilic polymer (co)), a positive point effect size will indicate that for the variable of interest being compared, the experimental, hydrophilic polymer has a greater value than the control while a negative point effect size will indicate the experimental, hydrophilic polymer has a lower value than the control. This is shown symbolically below:

*if e# > co, PES will be positive (+)*
if $e# < co$, $PES$ will be negative ($-\$)

*Equation 24: Interpretation of PES: Between Hydrophilic Polymers*

Comparisons made within a hydrophilic polymer (i.e. a swelling ratio value obtained after 3 days of swelling is compared to a swelling ratio value obtained after 1 day of swelling) follow a similar pattern. A positive point effect size will indicate for the variable of interest being compared that the value collected at a latter temporal value (e.g. 3 days) is greater in value while a negative point effect size will indicate the value collected at an earlier temporal value (e.g. 1 day) is greater in value). This is shown symbolically below:

\[
\text{if Day 3} > \text{Day 1, PES will be positive} \quad (+) \\
\text{if Day 3} < \text{Day 1, PES will be negative} \quad (-)
\]

*Equation 25: Interpretation of PES: Within Hydrophilic Polymers*

Statistically significant difference between groups being compared will be indicated by the 95% confidence interval containing the null value zero. In other words, if the 95% confidence interval upper and lower limits contain the same signage (i.e. both positive or both negative) there is a statistically significant difference between the data sets being compared whereas if the 95% confidence interval upper and lower limits contain differing signage (i.e. one limit is positive while the other limit is negative) there is not a statistically significant difference between the data sets being compared.

Tables, equations, and figures used throughout the thesis were created using Microsoft Office 2020 products such as Word and Excel due to their ease of usage and access.
Statistical Analysis

Degree of Conversion Statistical Analysis

DoC Normality Assumption

Each group was shown to fulfill the normality of distribution assumption by passing a Shapiro-Wilk test. As seen from Table 16, multiple Shapiro-Wilk tests produced p-values of 0.92, 1.00, 0.31, 1.00, and 0.93 for co, e2.5, e5.0, e7.5, and e10 respectively as shown in in the appendix. All of these are well above the assumed alpha of 0.05, therefore there is not enough statistically significant evidence to reject the null hypothesis that each sample comes from a normally distributed group.

DoC Homogeneity of Variance

After running the entire data set through a Brown-Forsythe test, a p-value of 0.4926 was produced as shown in Table 16 in the appendix. This is much higher than the assumed alpha of 0.05, therefore there is not enough statistically significant evidence to reject the null hypothesis that all groups possess homogeneity of variance.

DoC Point Effect Sizes, 95% Confidence Intervals, and Effect Sizes Percent Forms
When compared to co, as seen in Figure 3, e2.5 produced a point effect size of 1.7858 [4.6510, -1.0794, 96.29%], e5.0 produced a point effect size of 1.1427 [3.6715, -1.3862, 87.34%], e7.5 produced a point effect size of 0.7213 [3.0958, -1.6533, 76.46%], and e10 produced a point effect size of -3.3938 [0.6351, -7.4228, 0.03%]. The point effect sizes produced an average value of 0.0640±2.3464 and absolute versions of the point effect sizes produced an average value of 1.7609±1.1733.

**Thermal Degradation Statistical Analysis**

**Tdeg Normality Assumption**

The hydrophilic polymers within the data set, as seen in Table 17, were shown to have normal distributions through a series of Shapiro-Wilk statistical tests. As seen in the table, testing of all of the hydrophilic polymers produced p-values much greater than the assumed alpha of 0.05. This shows that there is not enough statistically significant evidence to reject the null hypothesis that each sample comes from a normally distributed group.
Tdeg Homogeneity of Variance

After running the entire data set though a Brown-Forsythe test as seen in Table 17, a p-value of 0.50 was produced. This is much higher than the assumed alpha of 0.05, therefore there is not enough statistically significant evidence to reject the null hypothesis that all groups possess homogeneity of variance.

Tdeg Point Effect Sizes, 95% Confidence Intervals, and Effect Size Percent Form

When compared to co, as seen in Figure 4, e2.5 produced a point effect size of -0.24 [2.03, -2.52, 40.42%], e5.0 produced a point effect size -0.08 [2.19, -2.35, 46.73%], e7.5 produced a point effect size of -0.48 [1.81, -2.77, 31.58%], and e10 produced a point effect size of -0.11 [2.16, -2.38, 45.57%]. The point effect sizes in original and absolute forms produced average values of -0.2288±0.1811 and 0.2288±0.1811 respectively.

Thermal Glass Transition Temperature Statistical Analysis

Thermal Glass Transition Temperature Normality Assumption

Each group was shown to fulfill the normality of distribution assumption as seen in Table 18 by passing a Shapiro-Wilk test. As seen from the table, multiple Shapiro-Wilk tests produced
p-values of 1.00, 1.00, 0.99, 1.00, and 0.99 for co, e2.5, e5.0, e7.5, and e10 respectively. All of these are well above the assumed alpha of 0.05, therefore there is not enough statistically significant evidence to reject the null hypothesis that each sample comes from a normally distributed group.

**Signal Change**

Each group was shown to fulfill the normality of distribution assumption by passing a Shapiro-Wilk test. As seen from Table 19, multiple Shapiro-Wilk tests produced p-values of 0.66, 1.00, 0.75, 1.00, and 0.93 for co, e2.5, e5.0, e7.5, and e10 respectively. All of these are well above the assumed alpha of 0.05, therefore there is not enough statistically significant evidence to reject the null hypothesis that each sample comes from a normally distributed group.

**Temperature Change**

Each group was shown to fulfill the normality of distribution assumption by passing a Shapiro-Wilk test. Multiple Shapiro-Wilk tests produced p-values of 0.69, 1.00, 0.36, 1.00, and 0.63 for co, e2.5, e5.0, e7.5, and e10 respectively as shown in Table 20. All of these are well above the assumed alpha of 0.05, therefore there is not enough statistically significant evidence to reject the null hypothesis that each sample comes from a normally distributed group.

**Tg Homogeneity of Variance**

**Thermal Glass Transition Temperature**

After running the entire data set through a Brown-Forsythe test, a p-value of 0.68 was produced as shown in Table 18. This is much higher than the assumed alpha of 0.05, therefore there is not enough statistically significant evidence to reject the null hypothesis that all groups possess homogeneity of variance.
Signal Change
After running the entire data set through a Brown-Forsythe test, a p-value of 0.95 was produced as shown in Table 19. This is much higher than the assumed alpha of 0.05, therefore there is not enough statistically significant evidence to reject the null hypothesis that all groups possess homogeneity of variance.

Temperature Change
As seen in Table 20, after running the entire data set through a Brown-Forsythe test, a p-value of 0.64 was produced. This is much higher than the assumed alpha of 0.05, therefore there is not enough statistically significant evidence to reject the null hypothesis that all groups possess homogeneity of variance.

Tg Point Effect Sizes, 95% Confidence Intervals, and Effect Sizes Percent Form

Figure 5: Interval Plot for Thermal Glass Transition Temperature
Figure 6: Interval Plot for Signal Change

Figure 7: Interval Plot for Temperature Change
**Thermal Glass Transition Temperature**

When co was compared to e2.5, e5.0, e7.5, and e10, point effect sizes of -0.3863 [1.8984, -2.6709, 34.96%], -0.6161 [1.6961, -2.9284, 26.89%], -3.2381 [0.0648, -6.5410, 0.06%], and -1.7711 [0.8488, -4.3911, 3.83%] respectively as seen in Figure 5. These effect sizes in their original and absolute forms produced overall average point effect sizes of -1.5029±1.3059 and 1.5029±1.3059 respectively.

**Signal Change**

As seen in Figure 6, the point effect sizes between co and e2.5, e5.0, e7.5, and e10 are 0.3387 [2.6192, -1.9418, 63.26%], -0.522 [1.7773, -2.8217, 30.08%], -0.4802 [1.8143, -2.7746, 31.56%], and -0.2613 [2.0136, -2.5361, 39.69%] respectively. The point effect sizes in their original forms produced an overall average point effect size of -0.2312±0.3968 and in absolute forms produced an overall average point effect size of 0.4006±0.1216.

**Temperature Change**

As seen in Figure 7, the point effect sizes between co and e2.5, e5.0, e7.5, and e10 were 1.1391[3.5581, -1.2799, 87.27%], 0.1338 [2.4026, -2.1349, 55.32%], 0.1460 [2.4152, -2.1232, 55.80%], and 0.1927 [2.4638, -2.0784, 57.64%] respectively. The point effect sizes in their original and absolute forms produced an overall, average, point effect size of 0.4029±0.4914.

**Solubility and Water Sorption Statistical Analysis**

**Normality assumption**

**Solubility**

To determine if both data sets fulfilled the normality of distribution assumption, each group within each data set was run though a Shapiro-Wilk test with an assumed alpha of 0.05. The solubility data set produced p-values of 0.13, 0.01, 0.58, 0.82, and 0.59 for co, e2.5, e5.0, e7.5, and e10. So as to ensure all the groups within the data set were normal as to allow statistical
analysis without unethically modifying the data, the entire solubility data set was transformed by a log transformation as shown in the equation

\[ Solubility_{transformed} = \log_{10}(Solubility_{original}) \]

After the solubility data was transformed to the values shown in Table 22, p-values of 0.45, 0.18, 0.85, 0.74, and 0.41 were produced by the Shapiro-Wilk test for co, e2.5, e5.0, e7.5, and e10 respectively. The p-values of the transformed solubility data set were all greater than the assumed alpha of 0.05, therefore there was not sufficient evidence to reject the null hypothesis that the samples came from normally distributed groups.

**Water Sorption**

The water sorption data set in its original form produced p-values of 0.20, 0.11, 0.17, 0.39, and 0.26 for co, e2.5, e5.0, e7.5, and e10 respectfully as shown in Table 23. The p-values for each hydrophilic polymer were greater than the assumed alpha of 0.05, therefore there was not sufficient evidence to reject the null hypothesis that the samples came from normally distributed groups.

**Homogeneity of Variance**

*Solubility*

The homogeneity of variance assumption for the transformed solubility data set was tested using the Brown-Forsythe test as shown in Table 22. The original solubility data produced a p-value of 0.40. but the test was repeated after transforming the solubility data to fulfill the normality assumption. The log transformed solubility data set produced a p-value of 0.73. The p-value of the transformed solubility data set was above the assumed alpha of 0.05, therefore there is not sufficient evidence to reject the null hypothesis that there is homogeneity of variance across all 5 groups of the dataset.
**Water Sorption**

The homogeneity of variance assumption for the water sorption data sets was testing using the Brown-Forsythe test as shown in Table 23. The water sorption test produced a p-value of 0.47. This is above the assumed alpha of 0.05, therefore there is not sufficient evidence to reject the null hypothesis that there is homogeneity of variance across all 5 groups of the dataset.

**Point Effect Sizes, 95% Confidence Intervals, and Effect Sizes in Percent Form**

**Transformed Solubility**

When compared to co, a point effect size of -0.58 [0.92, -2.08, 28.08%] was formed for e2.5, -0.46 [1.02, -1.95, 32.14%] for e5.0, -0.06 [1.40, -1.52, 47.63%] for e7.5, and -0.64 [0.86, -2.15, 25.95%] for e10 as shown in Figure 8. The point effect sizes produced an average point effect size of -0.44±0.26 and the point effect sizes in absolute form produced an average point effect size of 0.44±0.26.

![Figure 8: Interval Plot for Log Transformed Solubility](image-url)
When compared to co, a point effect size of 1.86 [3.67, 0.05, 96.87%] was formed for e2.5, 3.37 [5.79, 0.94, 99.96%] for e5.0, 3.72 [6.32, 1.13, 99.99%] for e7.5, and 6.16 [9.99, 2.32, 100.00%] for e10 as shown in Figure 9. The point effect sizes produced an average and absolute point effect size of 3.78 ±1.78.

Swelling Ratio and Density Statistical Analysis

Normality of Distribution

Density

As seen from Table 24: Required Assumptions Table for Density, the density values for each hydrophilic polymer produced a p-value above the assumed alpha of 0.05 when run through a Shapiro-Wilk test. Since all of the p-values of all groups within the density data set are above the assumed alpha of 0.05, there was not sufficient evidence to reject the null hypothesis that all of the samples came from normally distributed groups.
Swelling Ratio

As seen in Table 25, all combinations of “hydrophilic polymer” and “hour” produced a p-value above the assumed alpha of 0.05 when run through a Shapiro-Wilk test. Therefore, none of the combinations of “hydrophilic polymer” and “hour” show there is statistically significant evidence to reject the null hypothesis that all samples come from a population with a normal distribution of means.

Homogeneity of Variance

Density

After running the density data set through a Brown-Forsythe test, a p-value of 0.05 was produced as seen in Table 24:Required Assumptions Table for Density. Since this is not below the assumed alpha of 0.05, there is not sufficient evidence to reject the null hypothesis that there is homogeneity of variance amongst the groups of the density population.

Swelling Ratio

When the data from 48 hours of soaking in DIH₂O was grouped by hydrophilic polymer and run through a Brown-Forsythe test, a p-value of 0.4405 was produced as seen in Table 26. This is above the assumed alpha of 0.05, therefore there is not enough statistically significant evidence to reject the null hypothesis that there is homogeneity of variance amongst the groups within the 72 hour-swelling ratio data set.

Point effect sizes, confidence intervals, point effect sizes percentage forms

Density
As seen in Figure 10, the point effect sizes created when comparing the density values of co to the other 4 experimental hydrophilic polymers tend to vary in value. The comparisons produced point effect sizes of -0.20 [1.26, -1.66, 42.05%], 0.09 [1.55, -1.37, 53.69%], -0.46 [1.02, -1.94, 32.22%], and 0.09 [1.55, -1.37, 53.73%] when co was compared to e2.5, e5.0, e7.5, and e10 respectively. All 95% confidence intervals contain the null value zero therefore based on the experimental results there is not sufficient evidence to conclude there is a statistically significant difference in density values between the hydrophilic polymers.
**Swelling Ratio**

*Figure 11: Interval Plot for Swelling Ratio (Co, All Hours)*
Figure 12: Interval Plot for Swelling Ratio (All Hydrophilic Polymers, 48 Hours)

As seen from Figure 11 and Figure 21 through Figure 24, point effect sizes and 95% confidence intervals were calculated for each hydrophilic polymer which compared how swelling ratios values changed between hour 1 to 3, 3 to 5, 5 to 10, 10 to 24, 24 to 48, and 48 to 72.

All hydrophilic polymers showed a similar pattern in point effect size values. Within each hydrophilic polymer, the largest point effect size occurred when comparing the average swelling ratio after 1 hour of soaking in DIH$_2$O to the average swelling ratio after 3 hours of soaking in DIH$_2$O. Overtime, this point effect size rapidly dropped in magnitude, until about 10 hours of soaking in DIH$_2$O at which the swelling ratio tended to stabilize as seen how the point effect size
when comparing hour 5 to 10, 10 to 24, and 24 to 48 is 1.38, -0.27, and 0.2 for co, 2.39, -0.31, and 0.49 for e2.5, 3.57, 0.69, -0.51 for e5.0, 2.14, -0.10, and 0.06 for e7.5, and 1.81, 0.37, and 0.02 for e10.

The 95% confidence intervals varied widely depending on the hydrophilic polymer. For the comparisons made within co, only hours 1 and 3 showed statistically significant differences in average swelling ratios. For e2.5 and e5.0, the average swelling ratios at 1 and 3 and 3 and 5 showed statistically significant differences in average swelling ratios. Experimental, hydrophilic polymer e7.5 showed statistically significant differences in average swelling ratios when comparing the values at hour 1 to 3 and at hour 3 to 5. Every comparison made within e10 produced confidence intervals containing the null value zero therefore there is not sufficient evidence to declare statistically significant differences in any of the comparisons made within the e10 population.

The point where swelling equilibrium is reached, as indicated by a point effect size within ±0.07 or 47.5 to 52.5% range, changes depending on the hydrophilic polymer. Hydrophilic polymers co and e2.5 obtain swelling equilibrium by hour 48 as seen by how the point effect sizes from comparing hour 48 to 72 within each hydrophilic polymer are -0.02 [2.88 -2.91, 49.32%] and 0.05 [9.17 -9.07, 51.99%] respectively. Hydrophilic polymers e7.5 and e10 obtain swelling equilibrium by 24 hours as seen by how the point effect sizes from comparing 24 to 48 within each hydrophilic polymer are 0.06 [2.72 -2.60, 52.46%] and 0.02 [1.60 -1.55, 50.91%] respectively. Although e7.5 and e10 are out of the swelling equilibrium range when comparing the average swelling ratio at 48 hours to 72 hours within each hydrophilic polymer, 0.08 [4.10 -3.93, 53.38%] and -0.08 [1.69 -1.86, 46.63%] respectively, this is only by a value of 0.01 and therefore extremely close to be acceptable. Hydrophilic polymer e5.0’s lowest
magnitude in point effect size occurred during the comparison between hour 48 and 72 which produced a point effect size of 0.34 [1.91 -1.24, 63.21%], therefore the hydrophilic polymer never reached swelling equilibrium within the experiment.

Due to 4 of the 5 hydrophilic polymers showing swelling equilibrium, or at least extremely close to swelling equilibrium, at 48 hours, the average swelling ratios between the control and the 4 other experimental, hydrophilic polymers were compared at this time interval. Figure 12 shows co tended to have an average swelling ratio lower than the other hydrophilic polymers by 48 hours as seen by how all 4 of the point effect sizes are negative in value. The figure also shows that the experimental, hydrophilic polymers containing MPS had average swelling ratios of a much larger magnitude than the control and that the magnitude grew as the weight percentage of MPS increased and TEGDMA decreased. This is seen by how the control produced a point effect size of 1.75 [3.53 -0.02, 96.03%], 1.89 [3.72 0.07, 97.09%], 2.90 [5.11 0.68, 99.81%], and 3.82 [6.46 1.18, 99.99%] when compared to e2.5, e5.0, e7.5, and e10 respectively. The 95% confidence intervals show that the experiment only reveals that e5.0, e7.5, and e10 have statistically significantly different swelling equilibrium values than the control while not sufficient evidence has been shown to conclude there is a statistically significant difference in swelling equilibrium values between co and e2.5.

Gel Fraction Statistical Analysis
Normality of Distribution

As seen in Table 28, all combinations of “hydrophilic polymer” and “day” produced p-values above the assumed alpha of 0.05 after going through a Shapiro-Wilk Test. This showed there was not sufficient evidence to reject the null hypothesis that the distribution of sample means is normal for all groups,
**Sphericity**

Since each comparison of a day’s and the prior day’s average gel fraction values within a hydrophilic polymer is a pairwise comparison, there is only two levels of treatments within each comparison. Therefore, the sphericity assumption is automatically fulfilled.

**Homogeneity of Variance**

After analyzing the gel fraction data, the average gel fraction value at day 20, grouped by hydrophilic polymer, underwent a Brown-Forsythe test. A p-value 0.5078 was produced which is above the assumed alpha of 0.05 as shown in Table 29. Therefore, there was not sufficient evidence to reject the null hypothesis that all groups in each data set express homogeneity of variance.

**Point Effect Sizes, Confidence Intervals, and Point Effect Sizes in Percentage Form**

![Interval Plot for Gel Fraction (Co, All Days)](image)

*Figure 13: Interval Plot for Gel Fraction (Co, All Days)*
As seen in Figure 13 and Figure 25 through Figure 28, the largest point effect size for each hydrophilic polymer occurred when comparing the average gel fraction values of day 0 to day 1. This produced point effect sizes of -7.36 [-7.26, -7.45, 0%], -16.72 [-16.69, -16.74, 0%], -7.26 [-7.22, -7.30, 0%], -4.08 [-3.97, -4.20, 0%], and -7.09 [-7.06, -7.13, 0%] for co, e2.5, e5.0, e7.5, and e10 respectively, revealing a rapid dropping in average gel fraction value from day 0 to day 1. Control, hydrophilic polymer co reached a consistent gel fraction value by day 7 as shown by how the comparison between day 7 and day 20 produced a point effect size of -0.05 [-0.04, -0.05, 48.19%], but all 4, experimental hydrophilic polymers showed consistent gel fraction values by day 20 as shown by how the comparison between day 20 and day 22 produced point effect sizes of 0.00 [0.00, -0.01, 49.89%], 0.03 [0.04, 0.03, 51.35%], 0.04 [0.04, 0.03, 51.85%], 0.05 [0.06, 0.04, 51.85%], and 0.02 [0.02, 0.02, 50.66%] for co, e2.5, e5.0, e7.5, and e10 respectively.

Further analysis of the interval plots revealed a pattern of a small spike followed by a sudden drop in point effect size values for all hydrophilic polymers. For co, this is seen to occur
over days 4 through 7 by how the point effect size is -0.09 when comparing day 4 to day 5, -0.33 when comparing day 5 to day 6, followed by a point effect size of -0.15 for day 6 to 7. The other hydrophilic polymers show a similar pattern, but this occurs over days 5 through 7 as seen by how the point effect sizes change from -0.32 to -1.35 to -0.38 for e2.5, -0.04 to -0.45 to -0.13 for e5.0, -0.06 to -0.32 to -0.12 for e7.5, and -0.08 to -0.44 to -0.14 for e10.

Since all hydrophilic polymers were shown to reach consistent average gel fraction values by day 20, comparisons were made between co and the 4, experimental hydrophilic polymers at day 20 as shown in Figure 14. This led to point effect sizes of 0.88 [3.30, -1.55, 80.96%], 0.67 [3.03, -1.69, 74.97%], 0.54 [2.86, -1.79, 70.40%], and 0.51 [2.83, -1.81, 69.56%] being produced when comparing co to e2.5, e5.0, e7.5, and e10 respectively.

**Discussion**

**Degree of Conversion Discussion**

The four point effect sizes show that swapping 2.5 wt% of TEGDMA with MPS caused the average sample of e2.5 to have a higher degree of conversion than the bottom 96.29% of samples from the control population, this effect was not maintained across the other experimental, hydrophilic polymers. That is, the degree of conversion of e5.0 and e7.5 was greater than the bottom 87.34% and 76.46% of the control’s population, respectively. There was a drop in degree of conversion for e10. Detailed analyses revealed that the testing does not provide sufficient evidence to conclude there is a statistically significant difference in degree of conversion between the control and the experimental, hydrophilic polymers.

This pattern of a sudden increase in degree of conversion by swapping 2.5 wt% of TEGDMA with MPS followed by slight drops in degree of conversion with additional swapping.
of 2.5 wt% of TEGDMA with MPS until a sudden drop when there is 0 wt% TEGDMA and 10 wt% MPS is explained by differences in chemical structure of MPS and TEGDMA.

As hydrophilic polymers, such as dental resins, undergo free radical polymerization during photopolymerization, initiators rapidly react with functional groups of monomers which in turn propagate to form long polymer chains until termination is reached via combination or disproportionation. This makes initiator concentration and the functionality of cross-linking monomers very important since as the functionality of the cross linking monomers increases, there is a greater chance of propagation occurring rather than termination, allowing for higher degrees of conversion (Brazel, 2012). The TEGDMA monomer is difunctional due to the alkene groups located at each of the ends of its main chain whereas the MPS monomer is only monofunctional due to only one end of its main chain possessing an alkene group while the other end consists of 3 methoxy groups meaning that it is easier for TEGDMA to propagate than MPS, allowing for higher degrees of conversion to occur. Additionally, the high amount of ethers located in the main chain of TEGDMA give great flexibility to the monomer or any polymer chain it is part of. This would make it easier for propagating monomers or chains near the end of the free radical polymerization process to move through the polymer to continue growing. On the other hand, the multiple methoxy groups located at one end of the MPS monomer combined with the higher polarity than TEGDMA as seen through the ClogP values of the hydrophilic polymers decreasing as the weight percentage of MPS increases, would increase the chance of entanglement occurring. This would limit the mobility of polymer chains and monomers within a hydrophilic polymer as it cures and lower the degree of conversion.

The lack of statistically significant differences in degree of conversion values between the control and any of the other 4 experimental polymer types may be owed to the similarity in
composition of formulations. The high similarity in composition of formulations across all polymer types, i.e. 90 wt%, may allow a majority of all formulations to act similarly during the photopolymerization process. This may greatly outweigh the influence stemming from the differences of chemical structure of TEGDMA and MPS hence the lack of statistically significant differences.

**Thermal Degradation Discussion**

When analyzing the 4, point effect sizes produced when comparing co to the 4 experimental, hydrophilic polymers, no obvious relationship between the amount of MPS swapped with TEGDMA and thermal stability is apparent. The average sample of e2.5, e5.0, e7.5, and e10 are shown to have a higher temperature at which thermal degradation occurs, as indicated by a 5% loss in mass, than the lower 40.52, 46.81, 31.56, and 45.62% of the control polymer’s population respectively. Despite the rapid fluctuation in values, the point effect sizes do indicate that the exchange of TEGDMA with any amount of MPS in the hydrophilic polymer appears to cause a decrease in overall thermal stability. However, all 4, 95% confidence intervals contain the null value of zero and therefore there is not sufficient evidence to conclude there is a statistically significant difference in temperature at which 5% of mass is lost between co and e2.5, e5.0, e7.5, or e10.

These results make sense when we consider the high similarity in chemical composition for all hydrophilic polymers. Each of the hydrophilic polymer formulations explored contain 1560 [mg] of HEMA which makes up 78% of the total 2000 [g]. As shown in the literature, the maximum rate of decomposition for polyHEMA (pHEMA) occurs at 275 [C], matching the overall average temperature at which 5% of the total mass was lost for the data: 275.89 [C] (Demirelli, 2002).
Thermal Glass Transition Temperature Discussion

Thermal Glass Transition Temperature

The 4 individual point effect sizes reveal that the combination of MPS and TEGDMA in a hydrophilic polymer influence the glass transition temperature over two phases. This first phase occurs when exchanging MPS for TEGDMA while retaining a greater or equal weight percentage of TEGDMA in the polymer. The second phase occurs when the weight percentage of MPS is greater than the weight percentage of TEGDMA. This is shown by how the calculated point effect sizes involving e2.5 and e5.0 indicate that the average sample of e2.5 and e5.0 has a higher thermal glass transition temperature than the bottom 34.83% and 26.76%, respectively, of all samples from the control hydrophilic polymer’s population. The point effect sizes indicate that the average sample of e7.5 and e10 has a higher thermal glass transition temperature than the bottom 0.06% and 3.84%, respectively, of all samples created from the control hydrophilic polymer’s population. However, since all 4, 95% confidence intervals contain the null value zero, there is not sufficient evidence to conclude that there is a statistically significant difference in the thermal glass transition temperature based on weight percentage of MPS in a hydrophilic polymer.

Signal Change

The 4 individual point effect sizes reveal that the average sample of e2.5, e5.0, e7.5, and e10 has a greater signal change value than the bottom 63.31%, 30.15%, 31.56%, and 39.74% of samples within the control hydrophilic polymer’s population. This reveals that once the weight percentage of MPS is equal or greater than the weight percentage of TEGDMA, there is a decrease in the signal change value that tends to rebound back to a higher value once there is no TEGDMA remaining in the formulation. However, all 4, point effect sizes produce 95% confidence intervals that contain the null value zero. Therefore, the testing does not provide
sufficient evidence to conclude that there is a statistically significant difference in the signal change value between co and the 4 other experimental, hydrophilic polymers.

**Temperature Change**

The 4 independent effect sizes reveal that the average sample created using the e2.5, e5.0, e7.5, and e10 hydrophilic polymers experience the transition between rubbery and glassy characteristics over a larger temperature change value than the bottom 87.29%, 55.32%, 55.96%, and 57.64% of samples belonging to the control hydrophilic polymer’s population. The large temperature change value for the transition between the glassy and rubbery states suggests that MPS leads to an increase in heterogeneity in the network. However, all 4, point effect sizes produce 95% confidence intervals that contain the null value zero. Therefore, the testing does not provide sufficient evidence to conclude there is a statistically significant difference in the signal change value between co and the 4 experimental, hydrophilic polymers.

**Overall Thermal Glass Transition Analysis**

According to *Fundamental Principles of Polymeric Materials* by Christopher S. Brazel and Stephen L. Rosen, the thermal glass transition temperature generally depends on 5 factors: the free volume of the polymer, the attractive forces between molecules, the freedom to rotate about their bonds, the stiffness of the chains, and the chain length. Thus, differences in the molecular structure of TEGDMA and MPS contributed to the differences noted in the thermal glass transition values.

Increased polymerization would link the TEGDMA to other monomers, thereby limiting its natural mobility and raising the thermal glass transition temperature. TEGDMA already has a much longer chain length than MPS (14 to 9 atoms respectively), so even longer chain lengths would only increase the thermal glass transition temperature of the overall cross-linked network.
MPS on the other hand, would exist as smaller units within the overall cross-linked network and would be able to take advantage of free volume much easier than TEGDMA within the polymer.

TEGDMA and MPS are not the major components in any of the polymer formulations. Across all of the formulations, TEGDMA and MPS combined make up 10 [wt%] while the remaining 90wt% is the same composition for all of the formulations. HEMA is the major component at 78wt%. At almost 8 times the weight percentage of MPS and TEGDMA, HEMA has a much greater influence on the structure of the formulations used in this investigation. Therefore, HEMA plays a major role in the thermal glass transition temperature as shown by the Fox-Flory equation. This equation shows that as the weight percentage of a monomer increases, so does its influence on the thermal glass transition temperature (Brazel, 2012).

\[
\frac{1}{T_g} = \sum_i \frac{w_i}{T_{g,i}}
\]

*Equation 26: Fox-Flory Equation*

The similar values for signal change across all hydrophilic polymers are also explained by the weight percentage of components. The signal change value can be defined by the rule of mixtures which states that the mass ratios of components within a material impacts the specific heat capacity value of the overall polymer which is used in the calculation of the reverse heat flow curve. Similar to the Fox-Flory equation, this means that the similarity in composition of the hydrophilic polymer formulations used in this investigation would dominate the overall specific heat capacity value (Xie, 2016).

Although the effect sizes and confidence intervals reveal that there is not sufficient evidence to indicate a statistically significant difference between the control and experimental hydrophilic polymers in terms of temperature range over which the phase transition occurs, it is
very important to remember what the effect size represents. The effect size used throughout this thesis is also known as the standardized mean difference and gives more accuracy into the magnitude of the difference of the means between the groups by taking their standard deviations into account through using a pooled standard deviation. However, more is revealed when looking purely at the standard deviations. As noted in the results section, the control, which contains 10 wt % of TEGDMA and no MPS, has a much lower standard deviation than the 4 experimental, hydrophilic polymers which all contain some weight percentage of MPS. The hydrophilic polymer with the closest amount of variation is e10, but this is a factor of 2.66 greater than the deviation shown by co. The experimental, hydrophilic polymers e2.5, e5.0, and e7.5 have even greater standard deviations at 3.76, 4.17, and 6.15 factors greater respectively than co. This comparison suggests the following: 1) that TEGDMA and MPS can lead to heterogeneity in the polymer network and 2) TEGDMA is able to form more consistent connections, i.e. crosslinks than MPS; this observation is supported as follows: the standard deviation of co is much lower than e10 and the standard deviations increase as the weight percentage of MPS increases and TEGDMA decreases in the hydrophilic polymers containing both monomers: e7.5 > e5.0 > e 2.5.
**Water Miscibility Discussion**

The results of the water miscibility investigation show an inverse relationship between weight percent water that leads to degradation and weight percent MPS. In other words, as the weight percent of MPS increases, a lower weight percentage of water is required to cause the degradation of the hydrophilic polymer. The pattern is revealed in Table 9 by how the order for lowest to highest weight percentage of water required for miscibility begins with e10 at 44.04±1.32 [%] then e7.5, e5.0, e2.5, and finally co at 62.26±0.61 [%]. These results are explained, in part, by the differences in polarity of MPS and TEGDMA. Monomers with more polar end groups such as esters, carboxylic acid, hydroxyl, and urethane tend to have a higher miscibility in water (Park, 2012). Combined with the information from the calculated log P values that the polarity of the hydrophilic polymers used in this investigation tend to increase as the weight percentage of MPS increases and TEGDMA decreases, it makes sense that less water would be required for full turbidity as the weight percent of MPS increases.

**Solubility and Water Sorption Discussion**

**Solubility**

The differences in point effect sizes is explained by the post-photopolymerization reaction that occurs in the experimental hydrophilic polymers through the condensation reaction of their methoxy groups. This creates additional covalent crosslinks in the cured polymers as they are exposed to water, which may counter the degradation associated with hydrolysis. However, it is also understandable why this was not enough to be considered statistically significant. Crosslinking, in general, eliminates solubility since the plasticizing effect of water cannot overcome the covalent bonding formed through free radical polymerization, causing polymers to swell rather than break down (Brazel, 2012). Although these bonds can be broken via hydrolysis, the free radical polymerization process creates long polymer chains which would
have larger molecular weights, making it difficult for the chains to disentangle and escape the cross-linked polymer (Brazel, 2012).

**Water Sorption**

A variety of factors can be attributed to the water sorption of a polymer. The results of the water sorption investigation show a statistically significant difference in water sorption by swapping TEGDMA with MPS in a hydrophilic polymer’s formulation. One factor that influences water sorption is the degree of hydrophilicity in the polymer (Parthasarathy, 2012). Due to the crosslinking that occurs in the polymers during photopolymerization, the hydrophilic polymers used in this investigation swell rather than dissolve — the degree of swelling increases as the polarity of the solvent becomes similar to the polarity of the hydrophilic polymer (Brazel, 2012). This is supported by the water miscibility and calculated log P value results which show that swapping even 2.5 weight percentage of TEGDMA with the more hydrophilic MPS can cause dramatic changes in the water sorption. These results and the large values in water sorption levels is supported by previous literature such as Brannon-Peppas et al. These investigators reported that a significant change in the degree of swelling of pHEMA can occur even with small changes to the hydrophilicity of a system through the addition of comonomers (Brannon-Peppas, 1990).

Another factor that may influence the water sorption capabilities of the polymers is the cross-linking density (Brazel, 2012). Despite the ability of solvents to cause swelling within the cross-linked solutes of similar solubility parameters, this is not enough to overcome the covalent bonds formed during the cross-linking process. This turns the cross-linking density of a polymer into a limiter on how much it can swell. While previously listed experiments such as the degree of conversion and the thermal experiments indicate that changing the weight percentage of
TEGDMA and MPS in hydrophilic polymer do not create a statistically significant difference in property values such as cross linking density, this only indicates the initial cross linking densities of the samples without exposure to a polar source such as water. TEGDMA has a cross linking density that is highest prior to exposure to water and then should decrease over time due to hydrolysis. MPS though can form additional cross linking through hydrolysis-condensation reactions as other portions of the hydrophilic polymer degrades, meaning that its cross-linking density is highly dynamic with respect to time and water. This means that while many of the crosslinks formed during the initial curing process degrade due to hydrolysis, and therefore allow more swelling to occur, additional crosslinks occur in the experimental hydrophilic polymers as a result of condensation reactions. This makes the “MPS cross links” not as limiting toward swelling process since they are formed when the samples have already swelled therefore not locking the hydrophilic polymers into smaller, pre-swelling volumes while strengthening the overall structures to withstand the forces that the infusion of water create on the structures.

Swelling Ratio Discussion

Density

The lack of statistically significant difference in density values between the control and experimental hydrophilic polymers can be linked to the high similarity in composition of all 5 hydrophilic polymers despite each individual polymer containing a different weight percentage of TEGDMA and MPS.

Swelling Ratio

The change in swelling ratio values for all hydrophilic polymers with time reflects the changes in diffusion of DIH₂O into the polymer. As seen in Figure 11 and Figure 21 through Figure 24, the point effect sizes are positive but tend to decrease in magnitude with time as seen in the comparisons between hour 1 and 3, hour 3 and 5, and hour 5 and 10. This indicates that
not only did the swelling ratio increase with time, but that rate of change in swelling ratio also
decreased with time. This pattern makes sense when we consider the diffusion of DIH$_2$O into the
hydrophilic polymer samples is influenced by the concentration gradient between the DIH$_2$O
within each sample and the DIH$_2$O surrounding each sample while submerged in DIH$_2$O. At
first, there would be a large difference in concentration values of DIH$_2$O between the polymer
and the surrounding environment, causing a rapid influx of DIH$_2$O into the polymer. As DIH$_2$O
diffuses into the polymer, the concentration of DIH$_2$O inside the sample will increase, lowering
the concentration gradient of DIH$_2$O between the polymer and the environment and therefore
slowing the diffusion process.

The results of the swelling equilibrium experiment indicate that the weight percent of
MPS can influence the swelling capabilities of the hydrophilic polymers studied in this
investigation. The interval plots also show that hydrophilic polymers with higher weight percent
of MPS, such as e7.5 and e10, not only reach swelling equilibrium by 24 hours, a day earlier
than the hydrophilic polymers with little to no MPS such as c0 and e2.5, but are also able to have
higher swelling ratios as seen in Table 14 and Figure 12. The increase in swelling ratio reflects
the logic used in the water sorption portion of this thesis that even small changes in
hydrophilicity can cause significant changes in the swelling capabilities of pHEMA. The degree
of hydrophilicity of a polymer can influence its water sorption capabilities. As noted in the
current investigation, the inclusion of MPS increased the hydrophilic nature of the hydrophilic
polymers therefore increasing its swelling capabilities, and the “MPS cross-links” do not limit
swelling as much as those formed during the initial curing process (Brannon-Peppas, 1990)
(Parthasarathy, 2012). The increased rate of diffusion also supports this since permeability is
linked to the solubility parameter, which is based on the hydrophilic nature of the hydrophilic
polymers (Postel S. e., 2013) (Postel S. S., 2016). The highly polar DIH₂O will be able to
overcome the membrane of a more polar hydrophilic polymer samples much easier, allowing for
hydrophilic polymers such as e7.5 and e10 to reach swelling equilibrium much quicker than co,
e2.5, and e5.0.

**Gel Fraction Discussion**

All 5 interval plots that explored how average gel fraction changed over time within each
hydrophilic polymer showed a pattern of a large, negative, initial point effect size which
logarithmically increased over time until a large, negative spike in the point effect size value.
The large, negative spike occurred during the comparison between days 5 and 6 for the control
and days 6 and 7 for the experimental, hydrophilic polymers. The logarithmic increase in point
effect size for all 5 hydrophilic polymers is reflective of how over time leachables and ethanol
would gain enough thermal energy via the vacuum oven to escape the confines of the samples
causing a decrease in overall gel fraction and therefore negative point effect size. The
combination of a drop in diffusion as ethanol molecules left a sample and molecules deeper in
the samples requiring additional energy to escape the sample results in the logarithmic shape to
the curve. The large, negative spike in effect size that appears in all 5 hydrophilic polymers may
be reflective of larger molecules leaving the confines of the samples. The combination of the
ester groups located in the monomers within the hydrophilic polymer samples, such as HEMA,
TEGDMA, and MPS, with the hydroxyl groups located in the solvent, such as ethanol, methanol,
and isopropanol, may leave the hydrophilic polymers vulnerable to hydrolysis throughout the
experiment. As the polymer chains break down, the now free-floating chains may become
entangled within the hydrophilic polymers and require an influx of energy to overcome
secondary bonds and obtain mobility (Ferracane, 2006). Although the vacuum oven provided
thermal energy to the samples, the ethanol may have prevented sufficient thermal energy reaching these larger, entangled chains since the ethanol used some of the thermal energy to transition from a liquid to a gaseous state. Once enough ethanol evaporated from the samples, the entangled chains were able to obtain enough thermal energy to gain mobility and leach from the bulk hydrophilic polymer. The reason that the control hydrophilic polymer experienced the large, negative spike in point effect size 1 day before the experimental hydrophilic polymers could be related, in part, to MPS. After 7 days immersion in ethanol, sol-gel reactions in the MPS-containing could leading to additional cross linking which could hinder the ability of larger molecules to escape the hydrophilic polymer.

After the spike in point effect sizes, all 5 hydrophilic polymers were shown to fulfill the point effect size target goal of ±0.07 between day 20 and day 22 of drying in the vacuum oven. However, point effect sizes revealed that there were no statistically significant differences in average gel fraction values between the control resin and any of the experimental resins. It is also important to consider that these samples experienced thermal energy in the vacuum oven equivalent to what would be produced by the human body (32.2 °C). Future studies at higher temperatures may reveal the true gel fraction.
Overall Discussion of Case Study

The results of the investigations reveal that the minor compositional differences in the hydrophilic polymers did not lead to extensive statistically significant differences in the measured properties. None of the experimental hydrophilic polymers showed statistically significant differences in degree of conversion when compared to the control. The results from the four thermal investigations (thermal degradation temperature, thermal glass transition temperature, signal change value, and temperature range) showed no statistically significant difference between the experimental and the control, revealing that the ratio of TEGDMA and MPS did not influence thermal properties in a statistically significant manner. Experiments comparing the density values and gel fraction values of the experimental hydrophilic polymers with the control also indicated no statistically significant differences in density or the gel fraction of a hydrophilic polymer based on the ratio of TEGDMA and MPS.

Out of all of the experiments performed, only the results of the water sorption and swelling ratio at 48 hours show statistically significant differences. Both data sets showed statistically significant difference between the control and e5.0, e7.5, and e10 with point effect sizes and 95% confidence intervals for the water sorption data set at 3.37 [5.79, 0.94, 100%], 3.72 [6.32, 1.13, 100%] and 6.16 [9.99, 2.32, 100%] and for the swelling ratio at 48 hours data set at 1.89 [3.72, 0.07, 97.1%], 2.90 [5.11, 0.68, 99.8%], and 3.82 [6.46, 1.18, 100%] respectively. Both experiments also show a similar pattern through the point effect sizes which indicated that the amount of water sorption and volumetric increase due to swelling scaled with the weight percent of MPS in the hydrophilic polymer: e10 > e7.5 > e5.0 > e2.5 > control. However, only the water sorption data set shows statistically significant difference between the control and e2.5, producing a point effect size with 95% confidence interval of 1.86 [3.67, 0.05, 96.9%] while the
data set for the swelling ratio at 48 hours produces a point effect size with 95% confidence interval of 1.75 [3.53, -0.02, 96.0%] which is not statistically significant due the inclusion of the null value zero, albeit barely.

As discussed in the hydrophilic testing chapter, water sorption and swelling ratio both relate to swelling and are therefore influenced by factors such as hydrophilicity, crosslink density, and solubility. The results of the solubility experiment showed no statistically significant difference between the control and the 4 experimental, hydrophilic polymers. Although the factor alone did not have a statistically significant impact, the influence of solubility could have enhanced the differences in swelling when considered with more prominent factors such as hydrophilicity. Additionally, the degree of conversion experiment and thermal experiments were all influenced by the crosslinking density and presented non-statistically significant results, but these experiments only involved hydrophilic polymers whose cross-linking densities had not been modified after days of swelling in polar substances. The results of the calculated log P values and water miscibility experiment and previous literature support that the ratio of TEGDMA and MPS influence the overall hydrophilicity of a hydrophilic polymer which in turn can greatly influence the ability of a hydrophilic polymer to swell (Brannon-Peppas, 1990).
Rheological Experimentation

Important Note on the Rheological Chapter

Due to the Covid-19 pandemic, rheological testing could not be completed. Therefore, this chapter will focus on the benefits of rheological based testing, important properties related to rheology, and various experiments that can be performed using the concepts of rheology to identify properties and characteristics of polymers.

Example Rheological Experiments and Analysis

Time Sweep

One of the sweeps most commonly performed on a material during rheological testing is the time sweep. During a time sweep, a material is exposed to constant factors such as amplitude, frequency, and temperature and variables such as the storage and loss modulus are monitored over a fixed time. While this appears to be much simpler than the other sweeps discussed below, the time sweep is one of the most useful sweeps that can be performed.

One benefit of performing a time sweep is that the amount of time required for full recovery of a viscoelastic material can be determined. Often when using an instrument to perform tests on material, the material must be loaded into the machine so that it is secure during testing such as through clamps or compression. While these are generally applied lightly to the material so as to avoid damaging the sample prior to the testing, the combination of elastic and viscous properties in viscoelastic materials means that the material may not be able to instantly recover from the lightly applied forces. If a sweep, such as an amplitude or frequency sweep, was performed before the material was able to fully respond and recover from the previously applied forces, that material will respond to the combination of the previous forces and the forces currently being applied to the material. The impact of the delayed response can also accumulate when tests are chained together in rapid succession since every change in applied forces in every
test creates its own delayed response which can possibly carry over several phases of a test or entire tests. This can easily lead to misleading or non-repeatable results and inaccurate analysis since an unaware investigator may believe the results of each test exclusively reflect the response of the viscoelastic material to the factors in play during that testing process. The time sweep helps avoid this scenario by revealing to the user when the material has fully recovered from previously applied forces, as indicated by a constant storage and loss modulus for a set period of time. Once the recovery time has been determined, tests can be optimized to account for the delayed response such as by having several data points being collected at each independent variable level in order to create an average value or for a time sweep for double the recovery time duration to be performed between tests on the same sample as to allow chaining tests in rapid succession.

The time sweep is also well suited to track how the overall structure of a material changes due to chemical interactions. Many events such as swelling, oxidation, and gelation are able to influence the structure and properties of a material but are initiated through chemical-based interactions. These chemical interactions can be difficult to track since many factors such as polymerization kinetics and diffusion can occur over long periods of time while having key events take place quickly, i.e. fractions of seconds or minutes. Factors such as constantly stopping and restarting testing creates the risk missing key events. This creates the risk of gaps in collected data which give an incomplete picture of the properties of a material. The time sweep allows for greater control of factors such as temperature and mechanical forces on the material during testing which limits their influence and ensures the results are mainly based on the chemical interactions. Property values such as the storage and loss moduli can be tracked continuously whether the material is in a more liquid or solid state which greatly lowers the risk
of gaps forming in data and allows for key pieces of information, such as the gel point which indicates the beginning of the formation of the gel-like structure as a material cures. This information can be obtained even in the middle of a phase change. Additionally, rheological factors such as the storage modulus and the loss modulus are linked to factors such as structural integrity, cross linking density, homogeneity, and molecular mobility giving insight into interactions occurring deep in the polymer.

Figure 15: Example of a Time Sweep Being Used to Monitor Gelation

Amplitude Sweep

An amplitude sweep is when the amplitude (strain or stress) is constantly increased slowly overtime on the polymer sample while other variables, such as temperature and frequency, remain constant (Franck, 2004). This is represented through a figure depicting the storage modulus and the loss modulus vs. the increasing amplitude value.
Many key pieces of information about a polymer can be determined from an amplitude sweep. While a constantly ramping strain or stress can be applied to a material during an amplitude sweep, it will be assumed a ramping strain is applied on the material as this sweep is explained. One piece of information that can be gathered is the range of the Linear Viscoelastic Region (LVER). The LVER represents the range of strain values under which the material elastically, or not permanently, deforms its structure. This is represented on an amplitude sweep by the region where there is a constant value for the storage and loss modulus over a range of strain values. The end of the LVER is indicated by the appearance of another important piece of information: the yield strain. The yield strain is the maximum amount of strain that can be applied to a material before plastic, or permanent, deformation occurs to the structure of a material. This is indicated by a change in the storage modulus from a constant value, as shown in the LVER for the material, to a dramatic decrease in value (Dawn, 2017).

Knowing both the LVER and yield strain value are important because they can be used to indicate if a polymer is appropriate for a specific application, whether that be withstanding or breaking at specific stresses or strains. Other pieces that can be gathered from the storage modulus values recorded during the sweep include an indication of structural integrity, based upon the length of the LVER, and how the material breaks down once reaching the yield strain value, whether that be in a brittle or ductile fashion as indicated by a rapid or slow decrease in the storage modulus value after reaching the yield strain value. The loss modulus can also provide useful information such as by indicating changes to the structure of the material that may not be detected by the storage modulus. For example, microcrack formation may not be enough to initially impact the overall structural integrity of a material but can grow into greater issues with increasingly applied stresses, strains, or fatigue with time. While the formation of the
microcracks would not change the storage modulus, the loss modulus would increase in value since the microcracks allow for easier molecular motion and dispersion of energy. If microcracks are indicated in a polymer, the true yield stress or strain value is then not when the storage modulus suddenly drops in value, but when the loss modulus value increases since it is at that strain that plastic deformation of the material truly begins.

Figure 16: Example of an Amplitude Sweep Being Used to Monitor Yielding Strain

Frequency Sweep
Another type of rheological test that can be performed on viscoelastic materials is a frequency sweep. A frequency sweep is similar to the amplitude sweep except the frequency of the applied stress or strain is increased overtime while the amplitude and the temperature remain constant (Menard, 2015). It is important to perform an amplitude sweep prior to the frequency
sweep so that it can be assured that the applied strain or stress is not at or above the yield value which can damage the material prior to testing and therefore lead to misleading data being collected. The data is presented in a graph of the storage modulus and the loss modulus vs. frequency.

When analyzing a figure for a frequency sweep there are many key events to look for. One of the most obvious sources of information comes from determining if the storage modulus is independent or dependent of frequency. Due to the elastic nature of solid and solid-like materials, the storage modulus will tend to be independent of the frequency as the material is able to respond elastically to the applied stress or strain. Liquids and liquid-like materials act in a more viscous manner meaning that they are more influenced by time and therefore frequency.

A common usage of frequency sweeps is to determine if a material undergoes phase changes at different frequencies. While many materials will have a consistently dominant storage or loss modulus across multiple decades of frequency values, some materials will have storage and loss moduli that are dependent on frequency, but either increase or decrease in value at differing rates. This may result in the moduli swapping dominance depending on the degree of the frequency value such as silly putty, which acts more liquid-like at low frequencies and more solid-like at higher frequencies. This is critical information to know for materials that are exposed to a wide variety of frequency values, such as oils and hydrolytic fluids used in mechanical engines in production lines and vehicles.

If a material expresses a phase transition due to exposed frequency, additional information can be obtained from the crossover frequency. The frequency at which a material transitions between being more solid or liquid-like is known as the cross over frequency, as indicated by the
storage and loss moduli being equal in value at the said frequency. One piece of information gathered from the cross over frequency is the relaxation time. The relaxation time is the time it takes for the stress in a material to decrease to 37% of its initial value and is equivalent to the reciprocal of the cross over frequency (Brazel, 2012).

\[ t_{\text{relaxation time}} = \frac{1}{\lambda_{\text{cross over frequency}}}[\text{sec}] \]

Equation 27: Relaxation Time Equation

As revealed in Figure 17, polymers can be ranked on molecular weight or molecular weight distribution quantitatively based on the cross over frequency. This is possible since “The cross over frequency is inversely proportional to MW [molecular weight], while relative MWD [molecular weight distribution] information can be extracted from the slopes of the storage modulus and the loss modulus curves” (Spe, 1996). Therefore if we consider the crossover frequency to be a point of reference, any other polymer whose cross over frequency is located to the left of the reference point will have a higher molecular weight and to the right will have a lower molecular weight. This can be seen by how polymers with higher molecular weights more molecules to crossover have, making it quicker for a gel structure to form and therefore the storage modulus to increase in value. Also, any point above the point will have a narrower molecular weight distribution and any point below the point will have a wider molecular weight distribution. This can also be seen by how polymers with a higher storage moduli point will have a stronger structural integrity which is linked to the homogeneity of the polymer therefore a polymer with a higher storage modulus will have a narrower homogeneity. While this does not provide a quantitative value for a molecular weight or molecular weight distribution for a polymer, this is very useful when determining how changes to the molecular structure of a
material, such as a chemical reaction or the addition or subtraction of components, influence the materials molecular weight and molecular weight distribution.

![Diagram](Image)

**Figure 17: Frequency Sweep Indication of MW and MWD. Obtained without permission from Syranidou, 2017**

Frequency sweeps are also useful in determining if sedimentation may occur in a material. Many polymer-based products include additives, such as thickeners or colloids, so that the product can obtain desired property values. If a material acts more liquid-like, or a higher loss than storage modulus, at low frequencies, it becomes easier for the floating particles to move throughout the material and settle at the bottom of containers due to the force of gravity while at low frequencies, such as sitting in storage or on a shelf for long periods of time. On the other hand, if a material expresses a more solid-like structure, a higher storage than loss modulus, at low frequencies, these additives are more likely to remain dispersed over time since the more solid structure will better limit the additives’ mobility. This information is useful in determining the
shelf life of a product or if a product needs to be shaken prior to usage to ensure the product is able to perform its intended function properly.

**Viscosity Sweep**

A useful test to investigate the viscosity of a polymer is to generate a flow plot. The plot is created by applying either a ramping shear stress or shear rate to a polymer while under constant, desired environmental factors and measuring the corresponding shear rate or shear stress respectively. This test should be performed over several decades of applied shear stress or shear rate to ensure proper characterization of the material as discussed earlier in the chapter. While a plot of simply shear stress vs. shear rate or shear rate vs. shear stress can be used to depict the data, it is recommended to perform a log-log transformation on the values to better depict the data collected over several decades. The data collected can be analyzed by using a log transformation of newtons law as shown below

\[
\tau = \eta \dot{\gamma} \quad \therefore \log(\tau) = \log(\eta \dot{\gamma}) = \log(\eta) + \log(\dot{\gamma})
\]

*Equation 28: Log Transformed Viscosity Equation*

\[y = b + mx\]

Based upon the log transformed Newton’s law, the y-intercept of the log transformed flow plot represents the log transformed zero-shear viscosity of the material while a slope of one indicates that the material is Newtonian. Slope values greater or less than one indicate that the material expresses non-Newtonian properties since the linear relationship between shear stress and shear rate is not followed (Brazel, 2012). For a flow plot of log shear stress by log shear rate, if the log shear stress increases at a rate greater than the rate of log shear rate (i.e. the slope is greater than one) the results indicate the material has dilatant, or shear-thickening, properties while if the log shear stress increases at a rate less than the rate of the log shear rate (i.e. the
slope is less than one) the results indicate the material has pseudoplastic, or shear-thinning, properties. Bingham plastics appear similar to Newtonian fluids, possessing a slope of 1, but require a certain threshold of shear stress or shear rate applied to the material before it flows.

![Diagram showing different types of fluid behavior]

**Figure 18: Example of a Flow Plot Being Used to Determine Polymer Properties**

Some materials may even express a combination of Newtonian and non-Newtonian characteristics. As the applied shear stress or shear rate changes, thresholds may be met which allow for the molecular structure of the material to change, such as how chain disentanglement can lowering the overall viscosity value as the polymer chains align along the velocity gradient as shown in the example figure below. This is shown as viscosity vs shear rate and follows similar analysis rules for the shear stress vs shear rate example figure above where a true Newtonian fluid would show a constant viscosity value while a non-Newtonian fluid’s viscosity value will change based on applied shear stress or shear rate.
Figure 19: Example of Flow Plot Being Used to Depict Changes in Viscosity with Shear Based on Polymer Properties

In this example figure, the Non-Newtonian viscosity value can be divided into 3 regions: The Lower Newtonian Region (LNR), the Pseudoplastic Region (PR), and the Upper Newtonian Region (UNR). In the LNR, the polymer chains within the example non-Newtonian material are highly entangled. This entanglement allows the individual polymer chains to better resist the low, applied shear rate, resulting in a higher viscosity value which is labeled as the zero-shear viscosity value ($\eta_0$). As the applied shear rate increases in value, the chain entanglement is overcome, and the individual chains begin to align in the direction of the velocity gradient created by the applied shear rate. This causes the overall viscosity value to drop since as the chain entanglement drops so does the non-Newtonian material’s resistance to flow similar to a pseudoplastic material. Once enough shear rate is applied that the individual polymer chains fully untangle, the viscosity value for the material will once again be Newtonian like since the
minimal resistance to flow has been reached. The viscosity value of the UNR is named the infinite shear viscosity value ($\eta_\infty$).

Another type of flow plot that can be generated investigates if there is a time dependency for the viscosity of a material. The time dependent flow plot is generated by exposing the material in question to a constant shear stress or shear rate below the critical value at constant, desired environmental factors for a set time period. As the material is exposed to constant shear stress or shear rate, the viscosity value of the material should be measured and then used to generate a plot of viscosity vs time. If the material expresses constant viscosity value over the time period than the material is time independent, a property of Newtonian fluids, and if the viscosity value changes with time the material can be classified as non-Newtonian. Two types of non-Newtonian fluids that are time dependent are rheopectic and thixotropic materials. Rheopectic materials express a viscosity value that increases over time while under constant shear strain or stress while thixotropic materials express a viscosity value that decreases over time while under constant shear strain or stress. A key characteristic that applies to rheopectic and thixotropic materials is that when the constantly applied shear strain or stress is removed from the material, the material will recover to its original state as indicated by the viscosity value returning to its initial value given enough recovery time. When creating a time dependent flow plot it is important to show that the test has been repeated multiple times on the same sample, including recovery time between repeating tests, since a material that has been exposed to excessive shear stress or strain beyond the yield value will express thixotropic characteristics due to main chain breakage lowering the overall viscosity of the material. However, polymer chains that are plastically degraded do not recovery with time so later repetitions of the test will show the viscosity value not returning to its initial value even given excessive recovery time.
Figure 20: Example of Flow Plot Being Used to Explore How Viscosity Changes with Time

Performing viscosity-based testing on materials is extremely important because how a material’s viscosity value changes or does not change with applied shear stress or shear rate dictates its usage. Many products such as ointments or paints must be pseudoplastic since they must be able to easily spread over a surface with a hand or a brush to ensure uniform coating but be able to resist flowing once applied to the desired surface. Knowing the true viscosity characteristics of a product also prevents the product from being unintentionally damaged or incorrectly produced. For example, a specific shear rate may be applied to a product so as to avoid a critical shear stress value under the assumption the product is Newtonian. However, if the product is actually dilatant, or shear-thickening, the product may be exposed to more excessive shear stress than planned which can result in permanent damage. Another possible scenario is that if a product’s
viscosity is considered time independent when in reality it is thixotropic, or shear-thinning with time, the product may be assumed to be damaged and disposed of which would waste a lot of money and time in research or industry. Additionally, viscosity is tied to the molecular structure of a material and can therefore be used to investigate other factors which are known to influence the molecular structure such as thermal properties or the average molecular weight. This also gives great importance not just in learning the viscosity characteristics of a material but ensuring that collected viscosity values are correct since viscosity values can change rapidly even over a single decade of shear stress or shear rate.
Conclusion

Hydrophilic polymers are used across a wide variety of applications to solve problems that are both simple and complex, making hydrophilic polymers a common yet important part of our lives. Although the hydrophilic monomers that make up these polymers allows the final material to be used in wet environments, unpolymerized monomers as well as loosely crosslinked hydrophilic polymers may be susceptible to degradation via hydrolysis. In theory, the use of MPS in hydrophilic polymers could limit this degradation by using water to create additional cross linking via hydrolysis-condensation reactions. The additional crosslinking may counteract the vulnerability of hydrophilic polymers to degradation in wet environments. After performing many experiments which explored how various ratios of TEGDMA and MPS influence thermal and hydrophilic properties, with rheological testing unfortunately postponed due to the pandemic, the results showed that the only statistically significant differences created by the inclusion of MPS into a hydrophilic polymer appeared in experiments focusing on the swelling aspects of the resin: a water sorption experiment and a swelling ratio experiment. The point effect sizes, and 95% confidence ratios created when comparing the experimental resins containing various ratios of MPS and TEGDMA to a control resin that utilized only TEGDMA and no MPS revealed statistically significant differences. The water sorption data set revealed that the experimental resins e2.5, e5.0, e7.5, and e10 had average water sorption values greater than 96.9%, 100%, 100%, and 100% of the control resin populations respectively and that the water sorption capabilities increased as the weight percent of MPS increased so that e10 > e7.5 > e5.0 > e2.5 > co. The swelling ratio data at 48 hours revealed a similar pattern with the average swelling ratio values for experimental resins e5.0, e7.5, and e10 being greater than the bottom 97.1%, 99.8%, and 100% of the control resin population. Although the 95% confidence interval
created when comparing e2.5 to the control resin resulted in not enough evidence to conclude statistically significant differences in swelling ratio between the two hydrophilic polymers, the point effect size revealed that the average e2.5 sample had a higher swelling ratio value at 48 hours than the bottom 96.0% of samples within the control resin population. This once again reveals a pattern of e10 > e7.5 > e5.0 > e2.5 > co. Water sorption and swelling ratio are linked through swelling and both are therefore influenced by factors such as hydrophilicity, cross linking density, and solubility. The results of other experiments clarified the influence of these parameters, e.g. the results of the water miscibility experiment and calculated log P values supported a statistically significant increase in hydrophilicity as the weight percentage of MPS increased. The solubility experiment revealed there was not a statistically significant difference between any of the experimental resins and the control. Although the results of some experiments, e.g. degree of conversion and thermal experiments, were influenced by the cross-linking densities of the resins, there was not a statistically significant differences between the experimental and the control formulations. However, these experiments used samples that had not been exposed to highly polar solvents such as water or ethanol. Exposure to these solvents can influence the hydrolysis-condensation reaction and the cross-link density of the experimental formulation. Indeed, a variety of factors including solvents, temperature, composition, catalysts, pH and molar ratio of water/silane can influence the hydrolysis-condensation reaction. Solvents will influence the polymerization of silanes and the power of solvents is based on the following parameters: polarity, dipole moment and availability of labile protons. Therefore, the results indicate the differences in swelling capabilities may stem from differences in hydrophilicity in changes in the cross-linking densities over time based on the weight percentages of TEGDMA and MPS in the hydrophilic polymers.
The results also indicate ways in which the influence of MPS can be explored further. Investigations that explore the experimental formulations under environmental conditions that promote the hydrolysis-condensation reactions could answer some of the questions. Additionally, some results produced point effect sizes and 95% confidence intervals that with just a single additional sample per resin could have transitioned between being statistically significant and not being statistically significant or vice versa such as e7.5 of the thermal glass transition experiment (-3.24 [0.06, -6.54, 0%]), e2.5 of the water sorption experiment [1.86, 3.67, 0.05, 96.9%], and e2.5 and e5.0 of the swelling ratio experiment when comparing resins after 48 hours of swelling (1.75 [3.53, -0.02, 96.0%] and 1.89 [3.72, 0.07, 97.1%] respectively. Two more additional samples per resin for the water miscibility tests would also allow for point effect sizes and 95% confidence intervals to be generated providing more clarity on the hydrophilic nature of MPS and TEGDMA in hydrophilic polymers.
Works Cited


Coe, R. (2002). It's the effect size, stupid: What effect size is and why it is important.


Appendix
Degree of Conversion

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*Table 16: Required Assumption P-Values for Degree of Conversion*

Thermal Degradation

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*Table 17: Required Assumptions Table for Thermal Degradation*

Thermal Glass Transition Temperature, Signal Change, and Temperature Change

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*Table 18: Required Assumptions Table for Thermal Glass Transition Temperature*

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*Table 19: Required Assumptions Table for Signal Change*

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*Table 20: Required Assumptions Table for Temperature Change*

Solubility and Sorption

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### Table 21: Averages and SDs for Original Solubility Values

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### Required Assumptions Table for Log Transformed Solubility

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**Table 22: Required Assumptions Table for Log Transformed Solubility**

### Required Assumptions Table for Water Sorption

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<td>SW Test</td>
<td>0.20</td>
<td>0.11</td>
<td>0.17</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>BF Test</td>
<td></td>
<td></td>
<td>0.47</td>
<td></td>
</tr>
</tbody>
</table>

**Table 23: Required Assumptions Table for Water Sorption**

### Density and Swelling Ratio

### Required Assumptions Table for Density [g/cm³]

<table>
<thead>
<tr>
<th>Dental Resins (α=0.05)</th>
<th>Co</th>
<th>E2.5</th>
<th>E5.0</th>
<th>E7.5</th>
<th>E10</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-Values</td>
<td>SW Test</td>
<td>0.79</td>
<td>0.84</td>
<td>0.50</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>BF Test</td>
<td></td>
<td></td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>

**Table 24: Required Assumptions Table for Density**

### Normality of Distribution Assumption P-Values for Swelling Ratio

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>hour 1</th>
<th>hour 3</th>
<th>hour 5</th>
<th>hour 10</th>
<th>hour 24</th>
<th>hour 48</th>
<th>hour 72</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>0.83</td>
<td>0.40</td>
<td>0.52</td>
<td>0.45</td>
<td>0.40</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>e2.5</td>
<td>0.98</td>
<td>0.11</td>
<td>0.41</td>
<td>0.32</td>
<td>0.91</td>
<td>0.09</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>e5.0</td>
<td>e7.5</td>
<td>e10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>1.00</td>
<td>0.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.74</td>
<td>0.72</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.62</td>
<td>0.26</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.76</td>
<td>0.96</td>
<td>0.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.17</td>
<td>0.05</td>
<td>0.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.33</td>
<td>0.75</td>
<td>0.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.37</td>
<td>0.06</td>
<td>0.52</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 25: Normality P-Values for Swelling Ratio**

<table>
<thead>
<tr>
<th>Dental Resins (α=0.05)</th>
<th>Co</th>
<th>E2.5</th>
<th>E5.0</th>
<th>E7.5</th>
<th>E10</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-Values</td>
<td>SW Test</td>
<td>1.00</td>
<td>0.09</td>
<td>0.33</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>BF Test</td>
<td></td>
<td></td>
<td></td>
<td>0.44</td>
</tr>
</tbody>
</table>

**Table 26: Required Assumptions Table for Swelling Ratio (All Resin Types, 48 Hours)**

**Figure 21: Interval Plot for Swelling Ratio (E2.5, All Hours)**
Figure 22: Interval Plot for Swelling Ratio (E5.0, All Hours)

Figure 23: Interval Plot for Swelling Ratio (E7.5, All Hours)
Figure 24: Interval Plot for Swelling Ratio (E10, All Hours)

Gel Fraction

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Day -7</th>
<th>Day 0</th>
<th>Day 1</th>
<th>Day 2</th>
<th>Day 3</th>
<th>Day 4</th>
<th>Day 5</th>
<th>Day 6</th>
<th>Day 7</th>
<th>Day 20</th>
<th>Day 22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>avg 18.70</td>
<td>25.67</td>
<td>19.89</td>
<td>19.35</td>
<td>19.13</td>
<td>19.00</td>
<td>18.91</td>
<td>18.50</td>
<td>18.27</td>
<td>18.20</td>
<td>18.20</td>
</tr>
<tr>
<td></td>
<td>Sd 0.73</td>
<td>1.13</td>
<td>1.57</td>
<td>1.50</td>
<td>1.44</td>
<td>1.47</td>
<td>1.45</td>
<td>1.92</td>
<td>1.90</td>
<td>1.91</td>
<td>1.94</td>
</tr>
<tr>
<td></td>
<td>Sd 0.28</td>
<td>0.39</td>
<td>0.26</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>0.19</td>
<td>0.27</td>
<td>0.22</td>
<td>0.28</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>Sd 0.45</td>
<td>0.29</td>
<td>0.26</td>
<td>0.30</td>
<td>0.18</td>
<td>0.26</td>
<td>0.24</td>
<td>0.19</td>
<td>0.21</td>
<td>0.23</td>
<td>0.24</td>
</tr>
<tr>
<td>E7.5</td>
<td>avg 17.84</td>
<td>25.62</td>
<td>19.29</td>
<td>18.89</td>
<td>18.61</td>
<td>18.50</td>
<td>18.41</td>
<td>18.37</td>
<td>18.10</td>
<td>18.00</td>
<td>18.03</td>
</tr>
<tr>
<td></td>
<td>Sd 0.96</td>
<td>2.90</td>
<td>1.76</td>
<td>1.70</td>
<td>1.66</td>
<td>1.71</td>
<td>1.64</td>
<td>1.62</td>
<td>1.63</td>
<td>1.58</td>
<td>1.58</td>
</tr>
<tr>
<td>E10</td>
<td>avg 19.02</td>
<td>26.76</td>
<td>20.47</td>
<td>20.03</td>
<td>19.82</td>
<td>19.60</td>
<td>19.49</td>
<td>19.44</td>
<td>19.16</td>
<td>19.08</td>
<td>19.09</td>
</tr>
<tr>
<td></td>
<td>Sd 0.49</td>
<td>0.14</td>
<td>0.04</td>
<td>0.03</td>
<td>0.09</td>
<td>0.05</td>
<td>0.08</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 27: Averages and SDs for Gel Fraction (Original Form)

Normality of Distribution Assumption P-Values for Gel Fraction
<table>
<thead>
<tr>
<th>Resin Type (&lt;em&gt;α = 0.05&lt;/em&gt;)</th>
<th>Day 0</th>
<th>Day 1</th>
<th>Day 2</th>
<th>Day 3</th>
<th>Day 4</th>
<th>Day 5</th>
<th>Day 6</th>
<th>Day 7</th>
<th>Day 20</th>
<th>Day 22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>0.63</td>
<td>0.55</td>
<td>0.98</td>
<td>0.84</td>
<td>0.96</td>
<td>0.82</td>
<td>0.52</td>
<td>0.46</td>
<td>0.42</td>
<td>0.47</td>
</tr>
<tr>
<td>e2.5</td>
<td>0.25</td>
<td>0.48</td>
<td>0.78</td>
<td>0.82</td>
<td>0.73</td>
<td>1.00</td>
<td>0.15</td>
<td>0.94</td>
<td>0.21</td>
<td>0.64</td>
</tr>
<tr>
<td>e5.0</td>
<td>0.16</td>
<td>0.57</td>
<td>0.60</td>
<td>0.17</td>
<td>0.55</td>
<td>0.59</td>
<td>0.20</td>
<td>0.27</td>
<td>0.39</td>
<td>0.52</td>
</tr>
<tr>
<td>e7.5</td>
<td>0.42</td>
<td>0.29</td>
<td>0.26</td>
<td>0.18</td>
<td>0.42</td>
<td>0.15</td>
<td>0.14</td>
<td>0.25</td>
<td>0.25</td>
<td>0.18</td>
</tr>
<tr>
<td>e10</td>
<td>0.40</td>
<td>0.73</td>
<td>0.56</td>
<td>0.69</td>
<td>0.84</td>
<td>0.24</td>
<td>0.61</td>
<td>0.37</td>
<td>0.53</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Table 28: Normality of Distribution P-Values for Gel Fraction

<table>
<thead>
<tr>
<th>Required Assumptions Table for Gel Fraction (All Resins, Day 20)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dental Resins (&lt;em&gt;α = 0.05&lt;/em&gt;)</strong></td>
</tr>
<tr>
<td><strong>P-Values</strong></td>
</tr>
<tr>
<td><strong>BF Test</strong></td>
</tr>
</tbody>
</table>

Table 29: Required Assumptions Table for Gel Fraction (All Resins, Day 20)

Figure 25: Interval Plot for Gel Fraction (E2.5, All Days)
Figure 26: Interval Plot for Gel Fraction (E5.0, All Days)

Figure 27: Interval Plot for Gel Fraction (E7.5, All Days)
**Figure 28: Interval Plot for Gel Fraction (E10, All Days)**

### Statistical Analysis Code

#### Within a Resin Type

The code begins by using commands such as `clc`, `clear all`, and `close all` to ensure that previously run codes do not impact the current code’s results.

```matlab
clc
clear all
close all
```

The data for each experiment is then manually loaded into the code depending on the comparisons performed. If only comparisons are being made between resin types, the data is loaded into a matrix so that each column represents a resin type and the elements representing data points for each resin type. The columns are ordered left to right from lowest to highest weight percentage of MPS (i.e. co, e2.5, e5.0, e7.5, then e10).
Data sets from experiments involving comparisons between resin types and within each resin type are loaded so that each row represent samples for each resin type while each column represents the treatment level for each sample. The rows are blocked based on resin type with the row blocks ordered top to bottom from lowest to highest weight percentage of MPS (i.e. co, e2.5, e5.0, e7.5, and e10. The rows within each block represent a resin sample for the resin type. The columns are ordered left to right from lowest to highest treatment level for the experiment.

\[ \begin{array}{cccc}
\text{Co} & \text{e2.5} & \text{e5.0} & \text{e7.5} & \text{e10} \\
\text{S1} & ... & \text{Sn} & \\
\end{array} \]

\text{GF_data} = [1 1.392971246 1.080404686 1.04313099 1.034078807 1.025026624 1.022896699 1.014909478 1.001064963 1.000532481; 1 1.358974359 1.012263099 0.989409142 0.971014493 0.966555184 0.912486065 0.900222965 0.895763657 0.893534002; 1 1.365652398 1.094894275 1.068592058 1.052604435 1.04878597 1.041258381 1.035585353 1.02217638 1.018050542 1.020113461; 1 1.422067488 1.10230316 1.074450991 1.062131762 1.054097483 1.044991966 1.047670059 1.030530262 1.029459025 1.026780932; 1 1.424559471 1.105176211 1.078744493 1.066079295 1.057268722 1.053414097 1.047907489 1.035792952 1.028634361 1.029735683; 1 1.390860215 1.08655914 1.060752688 1.05 1.043010753 1.039784946 1.03333333 1.017741935 1.012365591 1.015053763; 1 1.444140197 1.098576123 1.077217963 1.069003286 1.052573932 1.045454545 1.048740416 1.032858708 1.026834611 1.026286966;]
Various values and empty variables are created to be used later in the statistical analysis process. The number of rows and columns in the data set are determined using the “size” function. For an experiment purely involving comparisons between resin types, the number of replications is equal to the number of rows in the data set. If the experiment involves comparisons between and within resin types, the number of replications for each resin type is equal to the number of rows in the overall data divided by the number of resin types in the experiment since this allows the number of replications per block to be obtained as shown below for the Gel Fraction analysis.

```
[rows columns] = size(GF_data);
replications = rows/5;
```

Various arrays are created to represent the labeling associated with each row and column in the total data set such as “Resin_Type_Time” which represents what treatment level is associated with each column and Resin_Type_Resins which represents what resin type is associated with each block of rows in the data set. The variable “alpha” is given the value of 0.05 to represent the assumed alpha of 0.05 to be used during later testing.
%number of replications for each treatment
alpha = 0.05;
Resin_Type_Time = [-7 0 1 2 3 4 5 6 7 20 22]';
Resin_Type_Resins = [0 2.5 5.0 7.5 10]';

Testing Within Each Resin type

Prior to comparing data values within each resin type, the data set representing the total data for the experiment is broken up into 5 smaller matrices, each representing a resin type block.

data_count = numel(GF_data);
Total_Data = GF_data;
Partial_Data(:,:,1) = GF_data(1:3,:);
Partial_Data(:,:,2) = GF_data(4:6,:);
Partial_Data(:,:,3) = GF_data(7:9,:);
Partial_Data(:,:,4) = GF_data(10:12,:);
Partial_Data(:,:,5) = GF_data(13:15,:);

Meas = Resin_Type_Time;

Empty matrices are then made to hold data values during the statistical analysis process.

These include “mixer” which will contain the data for each resin type block, “average” which will contain the average value for each treatment level in each block, and “SD” which will contain the standard deviation for each treatment level in each block.

mixer = [];
average = zeros(11,1,1);
SD = zeros(11,1,1);

The variable “Sorter” is set to a value of 1 so it can be used to organize the results of the statistical analysis later on.

sorter = 1;

All of the possible pairs of treatment levels are calculated by using the “nchoosek” function. This function takes all of the element values in the “Resin_Type_Time” array and forms pairs of elements so that no pair is repeated (e.g. day 1 and 3 and 3 and 1) as shown below.
\[ nCk = \frac{n!}{(n-k)!k!} \]

These pairs are placed in a 2-column matrix named “Possible_Pairs” with each row representing a pair of treatment levels in the data set. Since comparisons within a resin type are performed so that the data collected at a treatment level is only compared to the next treatment level, “Possible_Pairs” is modified accordingly.

```matlab
Possible_Pairs = nchoosek(Resin_Type_Time,2);
Possible_Pairs = Possible_Pairs(2:10,:);
Possible_Pairs(:,1) = Resin_Type_Time(2:10,1);
Partial_TSAS = zeros(length(Possible_Pairs),16,5);
assumption_book = zeros(5,1);
```

Next, Hedge’s d point effect sizes and 95% confidence intervals between a treatment level and the next treatment level is calculated within each resin type block. Required assumptions are not calculated for comparisons within a resin type since each comparison is a pair-wise comparison (automatically fulfilling the sphericity assumption) and the normality of distribution for each resin type-treatment level is calculated with an online Shapiro-Wilk calculator. This is all performed within a for-loop that cycles the value of variable “i” from 1 to 5 in intervals of 1 so as to allow each resin type block to be investigated. First, the resin type block based on the value of “i” is loaded into the empty matrix “mixer”. The functions “mean” and “std” are used to place the mean and standard deviation values for each treatment level in the matrices named “averages” and “SD” accordingly. To select the treatment levels to be compared, the variables “a” and “b” are used. The treatment level for variable “a” is assigned through a for-loop where the value of “a” changes from 2 to the second to last treatment level (e.g. column -1) in intervals of 1 and variable b is assigned a value of “a+1” to represent the next treatment level following “a”.

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Variable “a” starts at the second treatment level since the values in the first treatment levels for experiments involving repeated measurements of the same samples cannot be used in the statistical analysis calculations. The values in the first treatment level are useful to determine values such as the gel fraction or swelling ratio of samples and how they change with time. However, this causes the values with the first treatment level for all blocks to be the exact same value (e.g. 1 or 0 depending on the experiment). This makes it impossible to fulfill the required normality assumption and therefore cannot be used in the analysis process.

Variable “a” ends at the second to last treatment level since if “a” was assigned the last treatment level, there would be no treatment level to assign to “b” which would end the code prematurely. The pooled standard deviation value, named “spooled,” is calculated using the standard deviation values for each treatment level, located in the “SD” matrix, and the number of replications for each resin type. The variable “spooled” is then used with the “average” matrix to calculate the Hedge’s g point effect size, named “Hedges_g_sign.” This value is then corrected into a Hedge’s D point effect size, named “Hedges_D_sign,” to account for the upward bias that comes from using a small sample size within each comparison. An absolute form of the Hedge’s D point effect size is determined using the “abs” function and assigned to the variable “Hedges_D_Abs” which can be used to investigate the magnitude of the effect that the treatment level has on the sample. To calculate the 95% confidence interval for each point effect size, the t-distribution value and standard error must be known. The t-distribution value is manually assigned to the variable “tpaired” using student t tables based on the assumed alpha value and the degrees of freedom.
freedom for the comparison which is calculated using the equation below for comparisons within a resin type.

\[ df = \frac{n}{2} - 1. \]

The standard error is calculated by first placing the data values for treatment levels “a” and “b” inside the variables “x” and “y” respectively. Next, the difference in data values between each treatment level is calculated by subtracting array “y” from “x” is assigned the to the variable “di”. The “mean” function is then used on “di” to get the average difference value between treatment levels which is assigned to the variable “davg”. These are then used with “replications” to calculate the standard error for the comparison which is assigned to the variable “dsed.” The variables “tpaired” and “dsed” are then multiplied together to create a value which is assigned to the variable “CO_eff” which is then added and subtracted from the “Hedges_D_sign” value to determine the upper and lower values for the 95% confidence interval. These values are assigned to the variables “CI_upper” and “CI_lower” respectively. The values such as the average and standard deviation values for each treatment level, the Hedge’s g point effect size, the Hedge’s D point effect size in original and absolute form, and the upper and lower limits for the 95% confidence interval are then assigned to a row and dimension in the matrix “Partial_TSAS” based on the values of the variables “sorter” and “i” respectively, after which the variable “sorter” is then increased in value by 1. The for-loop for “a” then repeats until “a” is equal to the second to last treatment level, at which all desired comparisons between treatments levels have been performed and stored in individual rows of the matrix “Partial_TSAS.” The values of the 2-column array “Possible_Pairs” is then inserted into the first and second column of “Partial_TSAS” as to label which treatment levels are being compared in each row. The average and standard deviation values for the Hedge’s D point effect sizes in original form (column 11)
are stored in the first and second rows respectively in column 12 and absolute form (column 13) are stored in the first and second rows respectively in column 14 for the “i” dimension of “Partial_TSAS”. It is at this point the for loop for variable “i” ends and the loop repeats until “i” is equal to 5 in value, after which each resin type block has been analyzed and the results of the analysis for each block have been placed in an individual dimension of “Partial_TSAS.” Each dimension of “Partial_TSAS” is then placed in its own matrix (e.g. dimension 1 of “Partial_TSAS” which represents the resin block for resin type co is placed in the matrix “Partial_co_TSAS”) to make future analysis of each resin type block easier.

```matlab
for i = 1:1:5

    mixer = Partial_Data(:,:,i);
    average(:,:,i) = [mean(mixer)'];
    SD(:,:,i) = [std(mixer)'];

    [bf_p_value_partial, bf_stats_partial] = vartestn(mixer, 'TestType', 'BrownForsythe', 'Display', 'off');
    assumption_book(i,1) = bf_p_value_partial;

    sorter = 1;
    for a = 2:1:columns
        b = a+1;

        spooled = (replications - 1)*SD(a,1,i)*SD(a,1,i)+(replications-1)*SD(b,1,i)*SD(b,1,i);
        spooled = spooled / (replications + replications -2);
        spooled = sqrt(spooled);
        HedgesG_sign = ((average(b,1,i)-average(a,1,i))/spooled);

        HedgeD_sign = HedgesG_sign*(1-(3/(8*(replications-1)-1)));
        HedgeD_abs = abs(HedgeD_sign); % cohen D calculation:

        tpaired = 4.303;

        x = Partial_Data(:,:,b,i);
        y = Partial_Data(:,:,a,i);
        di = x-y;
        davg = mean(di);
        di_num = (di-davg).^2;
        d2vods= sum(di_num)/(replications-1);
        dsed = sqrt(d2vods/replications);
```

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\[
\text{CI.coeff} = \text{dsed} \times \text{tpaired}; \\
\text{CI.lower} = \text{HedgeD.sign} - \text{CI.coeff}; \\
\text{CI.upper} = \text{HedgeD.sign} + \text{CI.coeff}; \\
\]

\[
\text{Partial.TSAS}(\text{sorter}, :, i) = [0, 0, \text{average}(a, 1, i), \text{average}(b, 1, i), \\
0, 0, \text{SD}(a, 1, i), \text{SD}(b, 1, i), \text{HedgesG.sign}, \text{HedgeD.sign}, 0, \text{HedgeD.abs}, 0, \\
\text{CI.lower}, \text{CI.upper}]; \\
\text{sorter} = \text{sorter} + 1; \\
\]

\[
\text{Partial.TSAS}(::, 1, i) = \text{Possible.Pairs}(::, 2); \\
\text{Partial.TSAS}(::, 2, i) = \text{Possible.Pairs}(::, 1); \\
\text{Partial.TSAS}(1, 12, i) = \text{mean}(\text{Partial.TSAS}(::, 11, i)); \\
\text{Partial.TSAS}(2, 12, i) = \text{std}(\text{Partial.TSAS}(::, 11, i)); \\
\text{Partial.TSAS}(1, 14, i) = \text{mean}(\text{Partial.TSAS}(::, 13, i)); \\
\text{Partial.TSAS}(2, 14, i) = \text{std}(\text{Partial.TSAS}(::, 13, i)); \\
\]

\[
\text{Partial.co.TSAS} = \text{Partial.TSAS}(::, 1); \\
\text{Partial.e25.TSAS} = \text{Partial.TSAS}(::, 2); \\
\text{Partial.e50.TSAS} = \text{Partial.TSAS}(::, 3); \\
\text{Partial.e75.TSAS} = \text{Partial.TSAS}(::, 4); \\
\text{Partial.e10.TSAS} = \text{Partial.TSAS}(::, 5); \\
\]

**Between Resin Types**

Prior to performing comparisons between resin types, the overall data set must be reorganized. The goal for the reorganization is to resort the element values of the experimental data set so that each column represents a resin type, with the columns going from left to right in order of increasing weight percentage of MPS, while the rows are blocked based on the treatment levels of the experiment, with the blocked rows going from top to bottom in order of increasing treatment level. First, variables such as mixer, average, and SD are cleared and a new empty matrix called “Resin.Total.Data” is made to store the reorganized data. Next, a for-loop is used to input in data. By changing the value of the variable “reorg” from 1 to 5 in intervals of 1, a dimension of the matrix “Partial.Data” can be chosen based off of the value of “reorg” and assigned to the variable “holder.” The variable “holder” is then transformed from a matrix into an array assigned to the variable “Resin.Total.Data.Array”. The column
“Resin_Total_Data_Array” is then added to the matrix “Resin_Total_Data.” This continues until “reorg” is equal to 5 by which each resin block has been turned into a column array that is blocked by treatment level and added to the “Resin_Total_Data” matrix.

```matlab
clear mixer
clear average
clear commbo2
clear SD
mixer = [];
Resin_Total_Data = [];
average = zeros(5,1,1);
commbo2 = zeros(5,1,1);
SD = zeros(5,1,1);

for reorg = replications:replications:rows
    holder = Total_Data(reorg-2:reorg,:);
    Resin_Total_Data_Array = holder(:);
    Resin_Total_Data = [Resin_Total_Data Resin_Total_Data_Array];
end
Resin_Total_Day20=Resin_Total_Data(28:30,:);
```

With the data set now reorganized, values at specific treatment levels can now be compared between resin types such as how the gel fraction data at day 20 for all resin types as been placed in the matrix “Resin_Total_Day20”.

The statistical analysis for between resin types is very similar to the analysis performed within each resin type shown in the section above, but with minor changes. The first change is the fulfillment of required assumptions since comparisons within a resin type require normality of distribution and sphericity assumptions to be fulfilled while comparisons between resin types require normality of distribution and homogeneity of variance. The homogeneity of variance assumption was checked by using the “vartestn” function, which can be set to perform a Brown-Forsythe test on a data set. This functions then outputs a 1x2 matrix where the first element represents the p-value of the Brown-Forsythe test and the second element reports other statistical information such as degrees of freedom and the fisher statistic for the test. The second change is
recognizing that the groups being compared are different. Unlike when making comparisons within a resin type, where the data with a treatment level was compared to the data of the next treatment level, comparisons between resin types involve comparing the control resin to each of the other experimental resin types. This means that the “Possible_Pairs” matrix values and the values given to the variables “a” and “b” that are used when calculating the point effect sizes and confidence intervals should be changed to account for the new type of comparisons. This is done by using the array “Resin_Type_Resins” rather than “Resin_Type_Time” with the nchoosek function so that the “Possible_Pairs” matrix contains pairs based on resin types rather than treatment levels and setting up the values of “a” and “b” to change with nested for loops. Since there is only interest in comparing the control resin to the other experimental resin types, the outer for-loop keeps the variable “a” at a value of 1, so as to represent the control resin type, while the inner for-loop changes variable “b”’s value from 2 to 5 in intervals of 1 so as represent the other resin types. A third change is that the equation for confidence intervals changes for measurements between resin types. When the point effect size comes from a comparison between resin types, the degrees of freedom used to determine the t-distribution value changes from \((n/2)-1\) to \(2n-2\). Additionally, the standard error equation changes as shown below.

```matlab
[bf_p_value_between, bf_stats_between] = varstestn(Resin_Total_Day20,
'TestType', 'BrownForsythe', 'Display', 'off')
Possible_Pairs = nchoosek(Resin_Type_Resins, 2);
Possible_Pairs = Possible_Pairs(1:4,:);
Resin_Total_Statistical_Analysis_Storage = zeros(length(Possible_Pairs), 16, 1);

for i = 1:1:1
    mixer = Resin_Total_Day20
    average(:,:,i) = [mean(mixer)'];
    commbo2(:,:,i) = [mean2(mixer)'];
```
SD(:,:,i) = [std(mixer)'];

sorter = 1;

for a = 1:1:1
    for b = 2:1:length(Resin_Type_Resins)
        x = mixer(:,a,i);
        y = mixer(:,b,i);
        spooled = (replications - 1)*SD(a,1,i)*SD(a,1,i)+(replications-1)*SD(b,1,i)*SD(b,1,i);
        spooled = spooled /(replications + replications -2);
        spooled = sqrt(spooled);
        HedgesG_sign= ((average(b,1,i)-average(a,1,i))/spooled);
        HedgeD_sign = HedgesG_sign*(1-(3/(8*(replications-1)-1)));
        HedgeD_abs = abs(HedgeD_sign);
        tpaired = 2.776;
        SE =
        sqrt(((replications+replications)/(replications*replications))+(HedgeD_abs*HedgeD_abs)/(2*(replications+replications -2))));
        CI_coeff = tpaired*SE;
        CI_lower = HedgeD_sign-(tpaired*CI_coeff);
        CI_upper = HedgeD_sign+(tpaired*CI_coeff);
        Resin_Total_Statistical_Analysis_Storage(sorter,:,i) = [0 0 average(a,1,i), average(b,1,i), 0, 0, commbo2(a,1,i), SD(a,1,i),SD(b,1,i), HedgesG_sign, HedgeD_sign,0,HedgeD_abs,0, CI_lower,CI_upper];
        sorter = sorter +1;
    end
end
Resin_Total_Statistical_Analysis_Storage(:,1,i) = Possible_Pairs(:,2);
Resin_Total_Statistical_Analysis_Storage(:,2,i) = Possible_Pairs(:,1);
Resin_Total_Statistical_Analysis_Storage(1,12,i) = mean2(Resin_Total_Statistical_Analysis_Storage(:,11,i));
Resin_Total_Statistical_Analysis_Storage(2,12,i) = std(Resin_Total_Statistical_Analysis_Storage(:,11,i));
Resin_Total_Statistical_Analysis_Storage(1,14,i) = mean2(Resin_Total_Statistical_Analysis_Storage(:,13,i));
Resin_Total_Statistical_Analysis_Storage(2,14,i) = std(Resin_Total_Statistical_Analysis_Storage(:,13,i));
end
RSAS = Resin_Total_Statistical_Analysis_Storage(:,:, :) ;

RSAS_GF_Resin_Day20 = RSAS(:,:, 1);