Absorption of Various Small Organic Acid-water and Alcohol-water Solutions into Polyamide-11

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College of William and Mary

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Absorption of Various Small Organic Acid-water and Alcohol-water Solutions into Polyamide-11

A senior honors thesis submitted for a Bachelor of Science in Chemistry degree from The College of William and Mary

by

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_accepted for:____________________

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Abstract

Over many years, Dr. Kranbuehl’s lab has conducted an experiment monitoring the molecular weight of polyamide-11 as it is aged in different acid/water and alcohol/water environments. It was determined that different acids have different effects on molecular weight, and that methanol greatly increases degradation, while ethanol, though very similar in structure and properties, has no effect.

This leads to the study that is the focus of this thesis. Our goal is to determine if the reason some acids or alcohols have different effects on the polymer is because of the extent of diffusion into the polymer matrix. The theory is that depending on molecular size, not all acids/alcohols will be absorbed to the same extent and therefore not have the same opportunity to sever the polyamide bond.

We determine how different solutions are absorbed into the polymer by aging polyamide-11 beads in various acid and alcohol solutions. Acetic acid, propanoic acid, and butyric acid were chosen because they are present in varying degrees in crude oil, and are also very similar but with linearly progressing chain lengths. This allows us to see the effect of molecule size by increasing the length of the carbon chains off the acid group one by one. For the alcohols, ethanol and methanol were used because they are present in the pipes we study, and differ by chain length of one carbon yet produce greatly different effects on the degradation process.

The amount of liquid absorbed is measured using thermogravimetric analysis, and then it is possible to determine the relative composition of the liquid that was absorbed using the heats of vaporization measured with differential scanning calorimetry.
Introduction

Interests and Applications

Polyamide-11, abbreviated as PA-11, is a polymer composed of eleven-carbon monomer units joined by amide bonds. Though the polyamide of interest is a very specific material, other diverse types of polyamides, for the purpose of demonstrating its many types and forms, vary from Elmer’s™ glue (which is actually also PA-11), to biologically produced proteins. Proteins are synthesized naturally in living organisms, but are part of the same polymer family and could be called “PA-2” as the chains are two carbons long. They are composed of carbon-backbone chains joined with “peptide bonds”, which are synonymous with “amide bonds” but more commonly used for biological applications, while “amide bond” is a more general term. Therefore, naturally formed polyamides are referred to as polypeptides, while the synthetic counterparts are referred to as nylons or simply polyamides.

![Polyamide-11 structure](image)

Figure 1: Polyamide-11 structure

Our polyamide of interest, PA-11, has very different uses from polypeptides found in nature. Instead, this mid-performance synthetic material is used for applications such as sheaths for electrical wires, medical grade tubing, and lining for flexible pipes
used for off-shore oil rigs. This final application is the one of interest to our laboratory because these oil-pipe systems are extremely expensive, and when a pipe fails, the results can be catastrophic. Therefore, it is of the utmost importance for oil companies to analyze the PA-11 components to understand what levels of fatigue and aging can be sustained before failure occurs.

1. **Carcass**
An interlocking structure manufactured from a metallic strip. The carcass prevents collapse of the inner liner and provides mechanical protection against pigging tools and abrasive particles.

2. **Inner liner**
An extruded polymer layer providing internal fluid integrity.

3. **Pressure armour**
A number of structural layers consisting of helically wound C-shaped metallic wires and/or metallic strips. The pressure armour layers provide resistance to radial loads.

4. **Tensile armour**
A number of structural layers consisting of helically wound flat metallic wires. The layers are counter wound in pairs. The tensile armour layers provide resistance to axial tension loads.

5. **Outer sheath**
An extruded polymer layer. The function is to shield the pipe's structural elements from the outer environment and to give mechanical protection.

Figure 2: View of layers in NKT flexible pipe and description of each[^2]
The flexible pipes of interest contain multiple layers, each layer adding an important structural component to the system, each depicted in Figure 2. Multiple metallic layers allow the pipe to withstand very high pressures at the bottom of the ocean, add weight, and protect the pipe against abrasive particles in the mixture pumped through it. The polymer layers are used to protect the metallic parts against corrosion, and most importantly, maintain the integrity of the fluid within. Combined, these layers come together to form a pipe with the strength and weight of a steel pipe, but the flexibility and resistance to corrosion of a polymer pipe. Flexibility is important because the pipe is able to follow the contours of the seabed and avoid the complications involved with free pipeline spans. [1]

The degradation of these nylon pipe-liners is mainly the result of hydrolysis, where the polymer is exposed to water, which chemically severs the amide links. [3,4] As links are severed, the chain lengths, expressed in terms of molecular weight, decreases, resulting in embrittlement and eventual failure of the structure. The presence of acids catalyzes this process, as well as blocks the regeneration of these broken bonds. [5] The role of acids is of great concern because the crude oil pumped from the depths of the ocean contains naturally occurring small organic acids in a mixture of water and oil.

Because of this, our lab conducted an earlier study investigating a representative sampling of the acids present in the “produced-water” (the initial mixture of crude oil and water) to determine which acids have the greatest effect on the molecular weight, and therefore degradation, of polyamide-11. This was tested by aging PA-11 samples in different acid solutions at varying concentrations, then monitoring the change in
molecular weight through size-exclusion chromatography coupled with multi-angle laser light scattering techniques.

Degradation also occurs in the presence of methanol, which is significant for off-shore oil rigs because alcohols such as methanol are routinely pumped through the pipes in order to break up hydrates. A hydrate is a solid that forms in the rising liquid, which would clog the pipes and slow production if not dissolved. With this in mind, the experiment included methanol and ethanol systems in addition to the various acids.

The theory we are testing for why some acids or alcohols have greater effects than seemingly equivalent chemicals, is the molecules may not fit into the polymer matrix as well as others. This is a very important factor because the hydrolysis and recombination reactions occur very quickly, making the diffusion of the acid/water or alcohol/water solutions into the matrix a limiting kinetic factor. [5]

Thermogravimetric analyses of PA-11 samples aged in the different acid or alcohol solutions were performed in conjunction with differential scanning calorimetry in order to judge the quantity and composition of the solution absorbed into the polymer matrix. Data were collected throughout the aging process as well, in order to establish a general rate of absorption, rather than just a net absorption at the end of a cumulative period.
Chemistry of Polyamide Degradation

Hydrolysis

In a water environment, hydrolytic cleavage is the mechanism by which the polymer chains are “cut”. The mechanism requires the simultaneous attack of two water molecules to split the chain backbone at the amide bond (-CONH). One hydrogen from the first water molecule joins the NH, creating an NH$_2$ group. Simultaneously, a hydroxide (OH) from the other water molecule attacks the carbonyl (CO) carbon, creating an acid group (CO$_2$H), as shown in Figure 3. These simultaneous additions form a tetrahedral intermediate, which breaks down into a terminal amide (NH$_2$) and acid (CO$_2$H). [6] This occurs at a random point on the chain, wherever the water molecule finds its way into the backbone. It is therefore called “random chain scission”.[5]

Recombination

The above hydrolysis reaction is reversible however, in a type of polycondensation referred to as recombination because the two chain ends, being in the solid state, literally recombine again, releasing a water molecule. It is the same as random chain scission but in reverse. Scission leaves us with two chains, one with a terminal NH$_2$, the other with a terminal CO$_2$H. Through the same mechanism in the reverse direction, these end groups come back together to produce an H$_2$O, and the separate chains form the -CONH amide linkage and the two chains are one again. [6] It is also noteworthy that the recombination reaction occurs three orders of magnitude more quickly than the competing hydrolysis reaction. [5]
Figure 3: Mechanism for hydrolysis of polyamide-11 (forward reaction) and recombination (reverse reaction). [6]
Another important facet of recombination is the cage effect. This describes the concept that in a solid material, when a chain breaks, the structure of the material does not allow the two new ends to move around freely. Instead, they are “caged” together by the immobile surrounding chains. This greatly increases the chances of recombination, because the reactants retain their original orientation and spacing, which are essential for the reaction to proceed. [5]

Equilibrium

These two reactions, hydrolysis and recombination, are in a constant competition, each working in opposite directions. Every hydrolysis reaction breaks a bond and decreases molecular weight, while each polycondensation brings it back together, therefore increasing molecular weight. There is eventually an equilibrium between these two reactions, but when and where, in terms of molecular weight, depends on other variables such as fluid environment and temperature. [5]

In the initial stage of hydrolysis, the PA-11 chains are intact, and therefore the rate of recombination is minimal because there are no broken chains to be recombined. Therefore the rate of hydrolysis is much greater at the beginning of the aging process. As each hydrolysis reaction occurs however, a chance for recombination to take place is presented. This causes the rate of recombination to steadily rise as the concentration of adjacent acid and amide end groups rises as a result of hydrolysis, until an equilibrium is established where the rate of recombination has risen to match the rate of hydrolysis. At this point, the decrease and increase of molecular weight through opposing reactions are in balance, resulting in no net change in either direction. [5]
As in all chemical reactions, an increase in temperature increases the rate of both competing reactions, and therefore equilibrium is established much sooner. Temperature is a measure of the kinetic energy of a system, meaning the energy present from the motions of the individual particles. At increased temperatures, atoms are moving quicker, therefore increasing the rate of collisions with other atoms, and consequently the probability of colliding at the correct angles and proportions. Equilibrium between recombination and scission in polyamides is no different, and so elevated temperatures naturally cause the system to reach equilibrium much more rapidly. [5]

With this concept in mind, all aging performed in this study was carried out in a 90°C oven so that an equilibrium could be established on a much shorter timeline. The degradation that occurs in these pipes occurs over the course of many years, but the samples we aged at elevated temperatures (and higher concentrations of acids and alcohols) cut down the time required for the study to weeks or months instead.

\[
\text{CO}_2\text{H} + \text{NH}_2 \xrightarrow{\text{k}_p} \text{C-N} + \text{H}_2\text{O}
\]

Figure 4: Equilibrium between hydrolysis and recombination, with rate constant \( k_p \) for polycondensation and \( k_h \) for hydrolysis. [5]

**Acid Catalysis**

The presence of acids works against recombination [5] as well as acting as a catalyst and increasing the rate of hydrolysis. [7]

The rate of hydrolysis is increased at a lower pH because the acid is a very good \( \text{H}^+ \) donor, and protonates the carbonyl oxygen. As shown in Figure 5, this results in a
positive charge on the carbonyl carbon, making it much more susceptible to attack from a water molecule. [7]

Acids also lead to a greater extent of degradation because they can block recombination. As previously discussed, when a chain is hydrolyzed the amide bond breaks into an acid group and an amine group, which can recombine again by reforming the same amide bond that was broken. In an acidic environment however, the caged NH$_2$ group of a broken chain has the potential to react with acids from the medium rather than recombining by forming that bond with the acid from the polymer. This effectively caps the PA-11 chain because the polymer cannot recombine if an amide bond has already been formed with an acid from the medium.

Furthermore, recombination can be hindered as pH decreases because this means that the concentration of H$^+$ ions in the solution increases. These free protons can protonate the caged amine, which goes from NH$_2$ to NH$_3^+$. This terminal NH$_3^+$ group has less potential to react with the adjacent carbonyl, so the two caged ends are less likely to recombine. Therefore, acids are not only responsible for breaking the polymer chains; they also block the reactive sites on broken chains from coming back together, thereby driving equilibrium towards a lower molecular weight and increasing the rate and extent of degradation. [5]

For our study, it was important to know exactly which acids are present in the produced-water, because different acids behave differently. The oil companies themselves routinely analyze this mixture and report a wide variety of acids to be present. Certain acids were chosen to represent this variety in the earlier degradation study: acetic, valeric, napthenic, and cycloproanoic. Each of these have differing structures and
Figure 5: Mechanism for acid catalysis of hydrolysis in PA-11. [7]
properties, so a wide range of acidic properties were represented between all four. For this study of absorption however, we chose acids with a linear progression of chain size, in order to determine how each is differently absorbed. Therefore, acetic (2 carbons), propanoic (3 carbons) and butyric (4 carbons) were ideal, whose structures are given in Figure 6.

![Acetic Acid](image1.png) ![Propanoic Acid](image2.png) ![Butyric Acid](image3.png)

Acetic Acid $pK_a$ 4.76  
Propanoic Acid $pK_a$ 4.87  
Butyric Acid $pK_a$ 4.82

Figure 6: Structures and acidity values$^8$ for acids of interest

**Base Catalysis: Ethanolysis and Methanolysis**

As for the alcohols, methanol and ethanol sever the polyamide chain with similar mechanisms to the hydrolysis previously discussed, but can be thought of as base catalysts. Methanolysis has been reported to occur through the formation of an unstable tetrahedral intermediate on the carboxyl carbon, and it is reasonable to assume that ethanolysis occurs in the same fashion.$^9,10$ The addition to the carbonyl carbon is exactly the same as in regular hydrolysis, except that water is not contributing the $\text{OH}^-$ group. Instead, the entire conjugate base of the alcohol, methoxide ($\text{CH}_3\text{O}^-$) in the case of methanol, joins the carbonyl group to form the tetrahedral intermediate.$^9$ This intermediate dissociates into carboxylic acid (COOH) and an amine (NH$_2$) once again effectively cutting the PA-11 chain, as shown in Figure 7 depicting general base catalysis.
Figure 8: Mechanism for a general base catalysis of hydrolysis of PA-11. [9]
Although the same basic mechanism is proposed for both methanol and ethanol environments, we have shown in the earlier study that will be discussed shortly, that ethanol really has a minimal degrading effect, while methanol rapidly degrades the polymer. As members of the same family, they are very similar molecules, with ethanol just one CH₂ group larger than methonal, as shown in Figure 7.

![Methanol and Ethanol Structures](image)

**Figure 7: Structures for alcohols of interest**

The most likely explanation for why such similar molecules would have such drastically different effects on PA-11 is that the one additional CH₂ on ethanol is enough to either keep it from absorbing into the matrix, or cause a steric effect at the amide bond. CH₂ is non-polar and relatively large, so it seems to make a dramatic difference despite the relatively small molecular variation. The purpose of the alcohol experiment was to see how much ethanol was absorbed into the polymer matrix in relation to methanol absorbed because this would determine if diffusion into the matrix is limiting the reaction, or if there is a steric effect in forming the reaction intermediate structure.
Molecular Weight Study

This thesis work is an attempt to produce explanations to describe the results of a previous aging study, conducted over the course of many years with PA-11. The study monitored the molecular weight of PA-11 as it was aged in low concentration solutions of a representative sampling of the acids and alcohols present: cyclopropanoic acid, napthenic acid, acetic acid, valeric acid, methanol and ethanol. The molecular weight provides a measurement of the degree of degradation, as polymers that have been cut have a lower molecular weight, while intact polymers retain a higher molecular weight.

It was found that each acid influenced the hydrolysis process differently, and that methanol had a massive degradative impact on PA-11, while the very similar ethanol system had nearly no impact. This leads to my experiment, which would explain why similar compounds have such diverse effects on the polymer.

In the earlier experiment, molecular weights of the polymers were determined through two different techniques, then combined to get the most accurate data. We used the corrected inherent viscosity and size exclusion chromatography- multiangle laser light scattering. I will explain the basic concept behind how each technique produces a molecular weight value, but as it is a separate experiment from the thesis work, the details and exact procedure will not be discussed.
Instrumentation

Size Exclusion Chromatography- Multiangle Laser Light Scattering

The first technique is a direct measure of molecular weight through size exclusion chromatography, coupled with a multi-angle laser light scattering detector. This is referred to as SEC-MALLS.

In an SEC-MALLS system, the size exclusion column has the function of physically separating an injected liquid sample as it is forced through at high pressure. PA-11 is a solid, but samples can be dissolved in hexafluoroisopropanol (HFIP), which is an ideal solvent for this form of liquid chromatography.\textsuperscript{[11]} A small volume of a low concentration polymer sample is injected into the SEC column, which is packed with small porous beads. In addition to the pores in the beads themselves, the random arrangement of the beads also inherently leads to a diverse range of cavities and path lengths because of the varying gap sizes between adjacent beads.

This allows for a separation of polymer chains based on their size. Note however, that the “size” of the molecule does not refer to the actual length of the polymer chain. Size refers to the hydrodynamic volume, which is the amount of space that the chain takes up when it is randomly coiled in solution.\textsuperscript{[11]}

The largest polymer chains elute first because they are too large to pass through the beads and instead must take the quicker route around the outside. The smaller polyamide chains have more trouble passing through the column and are eluted last because they are small enough to fit into the tiny pores and therefore have a longer path length to travel as they weave through the bead itself rather than the direct path around it.
This difference in retention time depending on size of the chain effectively sorts the sample into a gradient from greatest to least hydrodynamic volume. After the sample is fractionated according to chain length, MALLS is used to determine the chain length of each fraction.

This operates on the principle that we can use the angle at which light is scattered from these very dilute solutions, and extrapolate the theoretical angle at which light would scatter for a zero concentration solution. This zero concentration value is very important because it is the inverse of the molecular weight of the polymer in the dilute solution.

**Corrected Inherent Viscosity**

The second technique that was employed was corrected inherent viscosity (CIV) determinations. This is a straightforward concept, in which the viscosity of a dissolved sample is related to the molecular weight based on the fact that as chains decrease in length, the solution will decrease in viscosity because the particles are smaller and are therefore able to flow easier.

To calculate this value, the sample is first dissolved in m-cresol and then poured into an Ubbelohde viscometer. Suction is applied to the viscosity tube to draw up the solution, and then the time it takes to flow through the tube is recorded. This number alone means very little, but it is useful when it is compared to the time it takes for the clean solvent (m-cresol) to flow the same distance in the same viscometer at the same temperature. To keep temperature constant, all of the viscosity runs are conducted in an oil bath held at 20°C. It is extremely important to keep each run at 20°C because
viscosity is highly dependent upon temperature. A cooler temperature was chosen because this increases the time measurements, therefore leading to greater accuracy as well as reproducibility.

The time to pass through the viscometer for the dissolved polymer solution divided by the time for the clean solvent gives the relative viscosity:

\[ \eta_r = \frac{t}{t_o} \]

where \( \eta_r \) is relative viscosity, \( t \) is time for the sample, and \( t_o \) is time for the clean solvent.\[11\] This is used to calculate the CIV, which is a relationship between the relative viscosity and the concentration of the polymer solution.

\[ \text{CIV} = \ln(\eta_r/C) \]

where \( C \) is the corrected concentration of the polymer solution. It is “corrected” concentration because it uses the polymer concentration \( (c) \), while taking into account the plasticizer content \( (p) \) of the PA-11 sample.\[11\]

\[ C = c(1-p) \]

A plasticizer is a substance that is added to a polymer while it is being made in order to increase the flow of the polymer so that less energy and time is required to make the material. We determine the plasticizer content via thermogravimetric analysis.

Now that we have the CIV of the sample, we can easily determine the viscosity average molecular weight (between number average and weight average) by using the Mark-Houwink relation:

\[ [\eta] = kM^a \]

Where \( M \) is molecular weight, and \( k \) and \( a \) are constants that can be looked up for a particular polymer, solvent and temperature combination.\[11\] The molecular weight can
also be determined by plotting the CIV data against the MW data obtained using SEC-MALLS.

**Results**

**Alcohol Results**

After the data was compiled, it was determined that methanol had a great effect, while ethanol had very little, as mentioned previously. This is interesting because they are extremely similar in structure and there is no obvious cause for this drastic difference. One theory is that they are absorbed into the polymer differently due to their difference in sizes. Ethanol is larger and could have more trouble entering the polymer, therefore reducing its ability to protonate the carbonyl as shown in Figure 5. The other option is that both could be absorbed at the same rate, but ethanol experiences a greater steric hinderance around the amide linkage, and is unable to react despite a reasonable concentration in the polymer.\[12\]
Figure 9: Results for methanol from molecular weight study \cite{12}
Figure 3.10: PA11 aging at 90°C in 30% EtOH and 100% DI water. The data was fit by the model described in this chapter.

Figure 10: Results for ethanol from molecular weight study \cite{12}
**Acid Results**

For the acids, cyclopropanoic had the most severe effect, while acetic had the least. This is not as surprising as the alcohol results, due to the fact that the acids varied in structure and properties. Size of the molecule does seem to have a very important role, indicating that the ability to be absorbed is a factor, as was also a possible hypothesis to explain the alcohol results. For the acids, this is demonstrated by comparing valeric and cyclopropionic acids, because both hydrophobic, but the larger molecule has less of an effect. The cyclopropionic system produced lower molecular weight, likely due to its smaller size since it is cyclic rather than a spread out chain. This supports the argument that absorbance into the polymer matrix is a major factor, and warrants further investigation.

This is why it is very important to determine in another experiment, the topic of this thesis, how different acids and alcohols are absorbed into the polymer matrix. These results will allow us to determine if diffusion is the key to the extent of reactions, or if exposure of the internal chains to the solvent is relatively constant, and the reactivity is simply different due to differences in steric hinderance.
Figure 4.6: The aging of commercial PA11 at 100°C in 600 ppm small carboxylic acid solutions.

Figure 11: Results for acids from molecular weight study \cite{12}
Absorption Study

Purpose

The results of the earlier degradation study indicate that the size of the acid molecule can play a very important role, first by changing absorbance into the polymer, or second, by creating steric hinderance around the amide bond. The goal of my experiment is to determine which of these hypotheses is correct. By choosing acids of similar properties, but with a linearly increasing carbon chain, we can determine the role that size of the acid plays in absorbance. Ideal choices for this were acetic (2 carbons), propanoic (3 carbons) and butyric (4 carbons), all shown in Figure 6. If absorbance is not affected, than the difference in effect on molecular weight must be a result of a change in reactivity, a steric effect, rather than a change in concentration in the polymer.

Ethanol and methanol systems are included in the experiment because the degradation study showed that they had drastically different effects, despite their very similar properties and pKa’s. The size of the molecule is the only significant difference, and therefore it is necessary to determine if the absorption into the matrix is the limiting factor, or if a steric effect at the amide bond. This is the same goal as with the acids. The structures for ethanol and methanol are given in Figure 7.

Materials

The PA-11 beads used were unplasticized and made by Aldrich [25035-04-5]. The acetic acid is glacial, produced by Fisher Scientific [64-19-7]. The butyric acid [107-92-6] is 99+% concentration, from Aldrich. The last acid is 99.5% propionic acid, also produced by Aldrich [79-09-4], though I will usually refer to it using the more common name of propanoic acid. The methanol is 99.9%, CAS number [67-56-1], from Fisher
Scientific. The ethyl alcohol, which I refer to using the common name ethanol, is denatured and pure (200 proof), from Aaper Alcohol and Chemical Co.

**Sample Preparation**

First, solutions were prepared of each sample at various concentrations by mass: a 50% and a 75% for each of the three acids, and a 50%, 75%, and 100% were prepared for both ethanol and methanol. A 100% deionized water sample was also added to the acid as well as the alcohol study, meaning there were two total pure water samples. Each sample is treated the same, whether acid or alcohol, so a water sample for each may seem redundant, but were necessary as they act as a check for reproducibility.

Each of the 14 resulting solutions were made to about 200 mL to act as a stock solution so the sample solution could be replaced with every run during data collection. The solutions were poured into 14 pressure tubes.

Fourteen sets of twenty-five unplasticized PA-11 beads were counted out and dried for one hour in a 100°C oven to drive off any moisture from the atmosphere. The beads were weighed together, then divided by 25 to obtain an average mass of each dry bead. Each set of 25 beads are put into the pressure tubes with the solutions, and are extracted and weighed together regularly to establish a general weight gain pattern throughout the study.

An additional 14 sets of 15 beads each were folded into metallic-mesh envelopes and placed in the corresponding pressure tubes as well, with the acid or alcohol solutions and the set of 25 weighed beads. The purpose of the mesh envelope is to keep them separate from the 25 other beads, as allowing them to mix would confuse the previously mentioned weights. The beads in these envelopes are present for use of TGA and DSC.
The weighed beads could not be used for these tests because if beads were removed and used, the average weights would not be consistent.

The final setup has each pressure tube, as shown in Figure 12, containing a particular concentration of acid, alcohol, or pure water, in addition to 25 weighed beads and 15 beads in an envelope set aside for testing. Each pressure tube is placed in an oven at 90°C to begin the aging process.
The testing can be divided into two main techniques: thermogravimetric analysis, and differential scanning calorimetry. These are used to determine the total amount of liquid that was absorbed into the matrix, as well as the composition of this liquid.

**Instrumentation**

**Thermogravimetric Analysis**

Thermogravimetric analysis, TGA for short, is a very important technique to determine the contents of a polymer sample. Ours is a model Q500 from TA Instruments and is pictured in Figure 13. The TGA is simple in concept: it is basically a furnace with a precise scale that measures weight loss as the sample is brought to temperatures at which the contents will degrade, or in the case of this experiment, just high enough to drive off any volatile content.

This is accomplished by chopping up a small amount of a polyamide sample in order to increase surface area and therefore the ease of volatile components to escape. These pieces are put on a small sample holder, which is dangled on a thin wire hook on the TGA. The sample holder is a pan made out of platinum because it is inert and easy to clean. Before each sample run, the platinum pan is held over a Bunsen burner in order to sanitize it. A picture of the platinum pan is provided in Figure 14.

This pan is suspended from a sensitive microbalance called a thermobalance, with the last digit on the order of a microgram. Such a level of precision is possible because mass is monitored using two photodiodes. Very small changes in mass cause a deflection in the beam between the diodes, and the imbalance in the photodiode current
Figure 13: TGA setup

Figure 14: Closer view of pan
is amplified in a magnetic coil, and transformed into mass data.\cite{13}

A furnace capable of reaching 1000°C is raised up around the pan suspended from the microscale. We used a temperature program where the temperature is held constant at the starting temperature in a 5 minute isotherm step, followed by a temperature ramp of 1°C/min to 185°C. This program was made to exactly match that of the DSC because the TGA is more flexible and using the same program for different techniques simplifies the process of comparing the two. With this in mind, the reasoning for this program will be explained in the DSC discussion.

Nitrogen is an inert gas and is constantly flowed through the system in order to displace the atmospheric air. At higher temperatures, the samples will oxidize in the presence of air in the TGA furnace, and will skew the weight loss process as oxidation is a chemical reaction whose products will be driven off, therefore leading to a greater loss of mass that does not correspond to the volatiles of interest.

Thermogravimetric analysis is of particular importance in this study because the volatile content that is quantified in this case is the acid or alcohol solution that was absorbed into the polymer beads as they aged in the various solutions. Each PA-11 bead was dried in an oven before starting the study, and the exterior was thoroughly dried prior to loading the sample so as to not to include the weight of the moisture simply clinging to the surface and not absorbed.

A TGA was performed on a dried sample bead as well, in order to establish a zero value for weight loss of all the subsequent data points. The beads are unplasticized however, and so the weight loss measured was small enough to be within our range of error and therefore negligible. The fluid content of the dry bead is consequently
approximated as zero, and it can be assumed that no moisture from the atmosphere or fluid from production is present in the beads after drying.

This means that the total weight loss is what was actually absorbed into the polymer matrix while it aged submerged in the solution. The temperature of the TGA was also kept below the point at which the polymer itself would begin to degrade, but high enough (185°C) to boil off any water, acid, or alcohol.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Acetic Acid</th>
<th>Propanoic Acid</th>
<th>Butyric Acid</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Boiling Point (°C)</strong></td>
<td>118</td>
<td>141</td>
<td>164</td>
<td>65</td>
<td>78</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 15: Boiling points of liquids under investigation

The temperature of a TGA can be important because certain components will often boil off at different times. *Ideally*, an isotherm at 80°C would release any ethanol (boiling point 78°C) but leave all the water until an isotherm at 105°C, where all the water (boiling point 100°C) would escape. These two different chemicals would boil off at different temperatures, and therefore each would have a distinguishable and identifiable peak occurring at the temperatures corresponding to its boiling point. By integrating each peak, we would know the exact ratio of weight loss that was attributed to each liquid, which is our final goal.

However, in reality it does not actually happen this way because at increased temperatures, though they may be below the boiling range, extensive evaporation occurs for both components. The facts that it is in a solid matrix, and that the liquid itself is multi-component (except the 100% systems) also mean that the vaporization
characteristics of the absorbed fluid are unpredictable. The result is a lack of resolution between peaks and more of a long and gradual loss of weight across the temperature scale.

Determination of relative weights of each component, which can also be thought of as the concentration of the liquid, is therefore not possible with just the TGA. It provides the total amount of volatile liquid that was absorbed into the matrix by simply using the total weight loss over the entire process. This total volatile mass can be applied to the differential scanning calorimetry analysis however, to figure out the ratio of each component as will be discussed in the following section.

Figure 16 shows an example of the thermograms produced from TGA. This is a plot for the 50% acetic acid sample at day 35, with weight percent plotted against time shown by the green line. The second y-axis is temperature, giving the advantageous ability to correspond changes in mass with what is going on at that point in the temperature program. This is shown by the blue line; basically a visual representation of the 5 minute isotherm followed by a 1°C ramp to 185°C.

The weight change over time (green line) is the main concern because the precise percent of weight lost is the goal of this method. Here, the weight loss is 14.7% of the initial mass, and this value is very important because this quantifies how this solution is absorbed into the matrix. It is also used in analysis of the DSC data to calculate concentration of the liquid within the polymer.
Figure 16: Example of TGA run
Differential Scanning Calorimetry

Differential scanning calorimetry, or DSC, is a system used to measure the thermodynamic events that occur, once again as temperature is increased according to a set program. Data is obtained from the difference in heat flow between a sample and empty reference pan. [13] Our DSC is a model 2920 Modulated DSC from TA Instruments.

Figure 17: DSC instrument setup
The sample is prepared by chopping the polymer into very small pieces, then placing about 6-10 milligrams into a pre-weighed aluminum pan. A lid is placed on the pan, and then they are clamped together to hermetically seal the system.

The pan is loaded into special capsule on the instrument, which measures the heat absorbed by the sample in the pan as temperature is varied. The aluminum pan itself does not affect the measurements because an ideally identical aluminum pan is used as a reference, sitting in the same capsule as the sample pan. This way, any measurements recorded for the empty reference pan can be subtracted from the sample pan to give measurements for only the sample alone and disregard the pan it is enclosed in. Both of the pans are heated uniformly by the same thermoelectric disk, and monitored with a set of thermocouples. [13]
This technique is of particular use for this experiment because an endothermic event occurs at the temperature where the mixture of liquids boils off, for which a heat of vaporization is measured.

The temperature program used, as mentioned in the TGA discussion, is a hold at the starting temperature in a 5 minute isotherm step, followed by a temperature ramp of 1°C/min to 185°C. The initial isotherm step is to establish a baseline and make sure that the sample pan is at the same temperature as the reference pan. The next step is a relatively slow ramp up in temperature because a slow ramp rate increases resolution and accuracy of the data. The final temperature of 185°C was chosen because it is high enough above the greatest boiling temperature of the media under investigation (butyric acid at 164°C), but not high enough to degrade the polymer.

Because our DSC is modulated, a sinusoidal function is overlayed on the temperature program so that miniature heating cycles are performed while the overall temperature program is performed. This allows for more detailed data after it is broken into reversing heat flow and nonreversing heat flow using Fourier transform methods.\[13\] The analyzer then uses the mass of the sample in conjunction with the heat either absorbed or released from the sample during the procedure to calculate the energy per gram of any exothermic or endothermic reactions that may have occurred as temperature is varied.

The percent mass of volatiles present in the polymer, which we obtained from the TGA, is used as the percent mass of volatiles within the DSC sample for the same bead. By dividing the heat of vaporization for the total sample mass by this percentage, we easily calculate the heat of vaporization for the fraction of sample that is absorbed fluid
rather than polymer. This is important because we use the data for energy absorbed per gram to calculate the concentration of the liquid, and so our “sample” of interest is the liquid and not the polymer itself.

Assuming that the sample is not a 100% concentration, it has two components: the experimental acid or alcohol, and the other is water. Any liquid that was absorbed into the polymer must be an unknown mixture of these two components. The concentration of the mixture is unknown because it will not necessarily be the same as the medium concentration if the acid or alcohol does not diffuse into the polymer to the same extent as water. Because selective absorption is possible, we seek to know the concentration of the liquid within the polymer. We determine this using the literature values for heats of vaporization for each of the two pure components, and the experimentally determined heat of the vaporization of the unknown combination of those two components. We then interpolate to find the concentration of the unknown.

Figure 19 presents an example, where substance A has a heat of vaporization of 1000 kJ/g, and substance B has a heat of vaporization of 500 kJ/g. A 750kJ/g peak for a mixture of A and B would have to be 50/50 concentration because it lies exactly between the heats for the two pure substances.

This method does not provide an exact number for the concentration, but it does give us a relative comparison between systems to work with. The interpolated value is an approximation because these systems are mixtures potentially capable of exhibiting azeotropic behavior, and the heats of vaporization for liquids alone cannot be expected to be the same as the heat of vaporization for the same liquid being heated inside of the polymer matrix. With this in mind, the values for weight percentage are consistently high
and can rise above 100%, which reflects the lack of precision in this approach of a comparative nature.

![Heat of Vaporization for a Mixture of A + B](image)

Figure 19: Hypothetical example of concentration interpolation, assuming a linear-additive dependence

A precise quantification is not necessary though; we simply seek a value for general comparison between systems, such as less than, greater than, or roughly equal in concentration. It may also be helpful to know if the masses absorbed (found using the TGA) were of unexpected concentrations relative to the concentration of the medium the beads were aged in. A significant difference would indicate that some molecules are selectively absorbed out of the water (if concentration in the polymer seems higher than the solution it was aged in), or that water was selectively absorbed over the acid/alcohol (if the concentration in the polymer is lower than the outside concentration).

Literature values of each pure substance involved were found and verified by performing DCS runs on each pure liquid. The process for performing a DSC on a liquid
requires a slight variation in procedure: the lid of the pan is punctured so that when the liquid boils, the resulting gas can escape. Otherwise, pressure would build up and cause the pan to eventually rupture. In order to maintain consistency, the lids were punctured for every run, including solid samples. This means that the mass of the volatiles being boiled off are escaping, however this is acceptable for this experiment because only the first endothermic event, the vaporization of volatiles, is of concern. The mass loss resulting from the vaporization of the liquid only affects subsequent events that are no of concern.

Figure 20 shows an example of a DSC analysis. Similar to the TGA output, two y-axes are used: one displays the heat flow while the other displays temperature so that peaks can be visually associated with the corresponding points in the temperature program. The blue line represents temperature, while the green line is heat flow.

The heat flow axis is in units of W/g, where W is joules per second, and the scale is such that exothermic events are shown going upwards, and therefore the upside-down peaks are endothermic.

The first large endothermic event corresponds the sample taking in the energy required for the contained volatiles to boil. The red line is an integration of this peak using a curved background signal, yielding the precise number of joules absorbed per gram of sample in the pan.
Figure 20: Example of results from DSC run

Differential Scanning Calorimetry
Sample: 50% Acetic Acid 50% DI Water Day 35

Heat Flow (W/g)
Heat of Vaporization

30.65 J/g

Temperature

Time (min)

Exo Up

Temperature (°C)
Data Collection Procedure

Due to the length of time required for each TGA and DSC run, only a few beads could be tested each day. Therefore, a rotating schedule developed such that each system got a data point for the TGA, DSC, and average bead mass about once a week.

For each system, the pressure tube was taken out of the oven for about twenty minutes to allow it to cool down to room temperature. The reason for this is if we were to remove the beads at such high temperatures, any absorbed liquid could evaporate out of the matrix (or boil out for the alcohols, considering the oven temperature is above their boiling points).

After the tube has cooled, the envelope containing the testing beads is removed and a single bead is removed, dried, and cut with a razor blade into small fragments. Roughly one half to three fourths of the bead goes into a TGA. The remaining mass is used for the DSC.

Meanwhile, the envelope is put back into the pressure tube, and the 25 beads are removed. These are all dried, and then weighed on a standard laboratory balance. This weight is then divided by 25 to get the average bead mass, establishing another method to monitor the absorption. The goal of this mass measurement is not to gain quantitative values for weight gain from absorption because this is provided by the TGA data. The goal of monitoring the weight of these 25 beads is to establish a general weight gain pattern that is less time consuming that a TGA run. This saves time because at the earlier stages of the experiment, the masses were monitored using this method without running TGAs, until it was clear that the beads had aged long enough to gain valuable data from running the TGA as the primary data source.
The 25 beads are then put back into pressure tube, and it is refilled (to approximately half volume - about 30mL) with the proper stock solution. The pressure tube is then bubbled for about 20 minutes with argon in order to displace any air from the tube, then resealed and put back into the 90°C oven. This is an important step, because without displacing air with an inert gas, the oxygen in the atmospheric air would lead to oxidation of the samples during heating in the oven.

The 50% concentration systems were the primary focus for data collection because each data point requires hours of testing, and considering that the time scale for the aging process is one day, it is impossible to collect more than a few data points for any given day. Therefore, it was necessary to choose one concentration to be the primary focus of all acids and alcohols. This way there are more data points to compare between systems, and the other concentrations are used for comparisons within each individual acid or alcohol to establish a general relationship between concentration and absorption.
Results

Figures 21 and 22 display the weight gain of the 25 bead sample in each system where the weight (as a percentage of initial weight) is plotted against the time (in days) the system has been aging in the experimental environment. For each data point, TGA and DSC data were also collected. Examples of the output for each instrument are provided for 50% acetic acid in Figures 16 and 20.

Figures 23 and 25 are tables that show the values that have been determined from each instrument for each run, as well as the corresponding calculations performed. The red text in these tables is used to highlight the data for the greatest aged samples for the 50% solutions of each type of environment. The 50% systems are of particular interest because the most data is available for comparison at these concentrations.

The corrected heat of vaporization is calculated as the heat of vaporization from the DSC, divided by the percent weight loss from the TGA. This is done because the uncorrected heat of vaporization gives the heat for the full mass in J/g. If we multiply this value by 1 g total mass, we have the total joules required for vaporization. We then divide this by the fraction of mass in grams corresponding to the fluid, yielding J/g fluid rather than J/g polymer.

The last columns in Figures 23 and 25 are weight percents inside the polymer, which express concentration of the liquid absorbed. These values are not to be taken literally, as discussed in the DSC section, but rather are used for a general comparison between systems.

The formula used for calculating the weight % is as follows: [corrected heat of vaporization (J/g) - heat of vaporization of liquid water (J/g)] / [heat of vaporization of pure acid or alcohol (J/g) - heat of vaporization of liquid water (J/g)]*100.
This equation relates to Figure 19 where the concentration is interpolated using the pure liquid heats of vaporization. The heats of vaporization for water and the relevant pure liquid are points on the same line, plotting heat of vaporization against concentration (concentration is 0 for pure water and 1 for the pure experimental liquid). Using these two points, a linear equation is obtained, and then rearranged into the above equation to solve for the unknown concentration using the experimental heat of vaporization obtained from the DSC.

The weight % column for the beads aged in 100% systems are not provided because weight % cannot be calculated for these systems as it is a one-component system and results in dividing by zero in the above equation.

Figures 24 and 26 are plots of fluid content (from the percent weight loss columns of Figure 23 and 25, respectively) plotted against time. The point of these plots is to point out trends for absorbance based on hydrocarbon chain length of the fluid molecules.
Figure 21: 25 bead weight gain for alcohols
Figure 22: 25 bead weight gain for acids
<table>
<thead>
<tr>
<th>PA-11 Bead System</th>
<th>Time aged (days)</th>
<th>Heat of Vaporization (J/g) (DSC)</th>
<th>% Weight Loss (TGA)</th>
<th>Corrected Heat of Vaporization (J/g) [Heat of Vaporization % Weight Loss]</th>
<th>Weight % of Alcohol Inside the Polymer [* using literature values]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100% DI Water</td>
<td>17</td>
<td>36.5</td>
<td>2.7</td>
<td>1367</td>
</tr>
<tr>
<td>Ethanol</td>
<td>100% Ethanol</td>
<td>28</td>
<td>30.9</td>
<td>12.5</td>
<td>247</td>
</tr>
<tr>
<td></td>
<td>100% Ethanol</td>
<td>48</td>
<td>14.0</td>
<td>13.6</td>
<td>103</td>
</tr>
<tr>
<td>75% Ethanol 25% DI Water</td>
<td>22</td>
<td>69.8</td>
<td>11.7</td>
<td>597</td>
<td>97</td>
</tr>
<tr>
<td>75% Ethanol 25% DI Water</td>
<td>34</td>
<td>50.8</td>
<td>12.6</td>
<td>405</td>
<td>107</td>
</tr>
<tr>
<td>75% Ethanol 25% DI Water</td>
<td>50</td>
<td>28.0</td>
<td>12.2</td>
<td>229</td>
<td>117</td>
</tr>
<tr>
<td>50% Ethanol 50% DI Water</td>
<td>20</td>
<td>60.7</td>
<td>9.1</td>
<td>667</td>
<td>93</td>
</tr>
<tr>
<td>50% Ethanol 50% DI Water</td>
<td>36</td>
<td>53.7</td>
<td>9.5</td>
<td>565</td>
<td>98</td>
</tr>
<tr>
<td>Methanol</td>
<td>100% Methanol</td>
<td>30</td>
<td>4.0</td>
<td>12.3</td>
<td>33</td>
</tr>
<tr>
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<td>100% Methanol</td>
<td>51</td>
<td>3.9</td>
<td>12.7</td>
<td>31</td>
</tr>
<tr>
<td>75% Methanol 25% Water</td>
<td>28</td>
<td>96.9</td>
<td>9.6</td>
<td>1014</td>
<td>64</td>
</tr>
<tr>
<td>75% Methanol 25% Water</td>
<td>35</td>
<td>51.5</td>
<td>12.3</td>
<td>420</td>
<td>94</td>
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<tr>
<td>75% Methanol 25% Water</td>
<td>49</td>
<td>100.5</td>
<td>10.1</td>
<td>998</td>
<td>65</td>
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<tr>
<td>50% Methanol 50% Water</td>
<td>20</td>
<td>61.0</td>
<td>6.9</td>
<td>884</td>
<td>71</td>
</tr>
<tr>
<td>50% Methanol 50% Water</td>
<td>37</td>
<td>55.5</td>
<td>6.2</td>
<td>900</td>
<td>70</td>
</tr>
</tbody>
</table>

* [corrected heat of vaporization (J/g) - heat of vaporization of liquid water (J/g)] / [heat of vaporization of pure alcohol (J/g) - heat of vaporization of liquid water (J/g)]*100

<table>
<thead>
<tr>
<th>Heats of Vaporization for pure liquids:</th>
<th>water</th>
<th>ethanol</th>
<th>methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>2308</td>
<td>536</td>
<td>295</td>
</tr>
<tr>
<td>Literature</td>
<td>2258</td>
<td>838</td>
<td>1100</td>
</tr>
</tbody>
</table>

Figure 23: Tables for results for alcohols, and heats of vaporization for pure liquids
Figure 24: Change in fluid content over time for alcohols
### Heats of Vaporization for Pure Liquids

<table>
<thead>
<tr>
<th>Pure Liquid</th>
<th>Experimental</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>2308</td>
<td>2258</td>
</tr>
<tr>
<td>Acetic</td>
<td>260</td>
<td>395</td>
</tr>
<tr>
<td>Propanoic</td>
<td>665</td>
<td>434</td>
</tr>
<tr>
<td>Butyric</td>
<td>530</td>
<td>459</td>
</tr>
</tbody>
</table>

* [corrected heat of vaporization (J/g) - heat of vaporization of liquid water (J/g)] / [heat of vaporization of pure acid (J/g) - heat of vaporization of liquid water (J/g)] * 100

---

### Table for Results for Acids and Heats of Vaporization for Pure Liquids

<table>
<thead>
<tr>
<th>PA-11 Bead System</th>
<th>Day</th>
<th>Heat of Vaporization (J/g) (DSC)</th>
<th>% Weight Loss (TGA)</th>
<th>Corrected Heat of Vaporization (J/g) [Heat of Vaporization/% Weight Loss]</th>
<th>Weight % of Acid Inside the Polymer [* using literature values]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100% DI Water D20</td>
<td>20</td>
<td>31.3</td>
<td>2.5</td>
<td>1250</td>
</tr>
<tr>
<td></td>
<td>100% DI Water D41</td>
<td>41</td>
<td>37.4</td>
<td>2.7</td>
<td>1391</td>
</tr>
<tr>
<td></td>
<td>100% DI Water D42</td>
<td>42</td>
<td>30.2</td>
<td>2.8</td>
<td>1068</td>
</tr>
<tr>
<td>Acetic</td>
<td>75% Acid 25% Water D16</td>
<td>16</td>
<td>18.9</td>
<td>19.3</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>75% Acid 25% Water D34</td>
<td>34</td>
<td>39.3</td>
<td>20.6</td>
<td>191</td>
</tr>
<tr>
<td></td>
<td>75% Acid 25% Water D41</td>
<td>41</td>
<td>23.2</td>
<td>18.1</td>
<td>128</td>
</tr>
<tr>
<td></td>
<td>50% Acid 50% Water D15</td>
<td>15</td>
<td>26.2</td>
<td>11.4</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td>50% Acid 50% Water D20</td>
<td>20</td>
<td>22.5</td>
<td>12.5</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>50% Acid 50% Water D29</td>
<td>29</td>
<td>26.8</td>
<td>12.9</td>
<td>207</td>
</tr>
<tr>
<td></td>
<td>50% Acid 50% Water D35</td>
<td>35</td>
<td>30.7</td>
<td>14.7</td>
<td>209</td>
</tr>
<tr>
<td>Propanoic</td>
<td>50% Acid 50% Water D20</td>
<td>20</td>
<td>25.4</td>
<td>17.8</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td>50% Acid 50% Water D36</td>
<td>36</td>
<td>29.5</td>
<td>18.7</td>
<td>158</td>
</tr>
<tr>
<td>Butyric</td>
<td>50% Acid 50% Water D17</td>
<td>17</td>
<td>14.1</td>
<td>21.3</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>50% Acid 50% Water D30</td>
<td>30</td>
<td>91.1</td>
<td>23.4</td>
<td>389</td>
</tr>
<tr>
<td></td>
<td>50% Acid 50% Water D35</td>
<td>35</td>
<td>106.0</td>
<td>28.0</td>
<td>379</td>
</tr>
</tbody>
</table>

---

Figure 25: Tables for results for acids, and heats of vaporization for pure liquids
Figure 26: Change in fluid content over time for acids

50% Acids: Changes in fluid content as a function of time
Discussion

Alcohols

Figure 24 most clearly shows the trend of absorbance between methanol and ethanol. For each concentration, grouped by color, the data for ethanol represented by circle markers, are consistently higher than the corresponding data for methanol (square markers of the same color).

This means that ethanol is more readily absorbed into the polymer than methanol. Not only is the percent weight loss measured by TGA higher, but also the DSC indicates that this fluid absorbed is actually of greater concentration as well. Because the ethanol has the greater concentration within the matrix, it has greater opportunity to react, and so it would be reasonable to assume that it would degrade the polyamide to a greater extent. This is the opposite of what actually occurs however, as established in the earlier molecular weight study. Ethanol actually has very little effect on polymer degradation, while methanol, despite the fact that is at a lower concentration than ethanol, greatly increases degradation relative to methanol.

The difference in chemical properties between methanol and ethanol is also small. They have similar $K_a$ values, and as discussed in the introduction, and interact with amides through very similar mechanisms. In fact, if the $K_a$ values are considered, ethanol is actually a slightly stronger base and would therefore be expected to have greater effect on degradation.

This indicates that methanol is more effective at inducing random chain scission due to steric differences between the two, rather than differences in concentration in the solid-state polymer. It is apparent that while the increased size of ethanol does not
prevent it from entering into the matrix, it *is* enough to cause enough steric hinderance at the amide bond to prevent the reaction from occurring.

**Acids**

The acids seem to be absorbed into the polymer based on chain length, as indicated by the correlation in fluid content in Figure 25, where the weight lost in the TGA increases as molecular size increases. Figure 26 shows this point clearly, as the data points for acetic acid (smallest molecule) are at the lowest fluid contents, propanoic in the middle-range, and lastly butyric (largest molecule) has the highest fluid content of all. This is the opposite of the expected relationship, and indicates that the longer the hydrocarbon chain of the organic acid molecule, the more it is absorbed into the polymer.

At first this seems odd because larger molecules should have more trouble flowing through the polymer structure as there is a greater chance of not fitting between the molecules in the matrix. However, the data tell us that the larger the carbon chain length, the higher the concentration. This can be accounted for when the chemical properties of adding carbons in series are considered relative to the structure of the monomer unit of the polymer chains. Each monomer segment contains a (CH₂) chain ten units in length attached to a carbonyl, then an amine. The acids also have the same basic structure, without the amine group. Therefore as the carbon chain length increases, the acid becomes increasingly similar to the polymer chain backbone. With this in mind, the larger acids with longer non-polar chains are able to diffuse into the similarly structured matrix more easily than the molecules with short carbon chains because “like dissolves like”. This reasoning can also be applied to the alcohols, explaining why the larger
molecules were absorbed to a greater extent at all concentrations than the smaller molecules.

Another interesting result for the acids was that the mass of the beads soaking in propanoic acid actually decrease in weight over time as shown in Figure 22. An increase in bead mass indicates that fluid was absorbed into the bead, which was the goal of the measurements. A negative weight gain however, was unexpected. It is interpreted as propanoic acid degrading or dissolving the polymer to a much greater extent than the others. By inspecting the solution, it was clear that the beads had indeed become extremely brittle and had fragmented in the solution, observable by the fact that the solution became cloudy and there were visible particles floating in the liquid. Thus, the beads were observed to be partially dissolving and fragmenting into the solution, therefore losing mass.
Future Studies

An addition to this study could be conducted with different acids and different concentrations. Acetic, propanoic, and butyric acid were chosen for comparison in this study because of their linear progression of sizes. Now, valeric and cyclopropanoic can be investigated as well because we have degradation information for each of these specific environments from the earlier molecular weight study. The goal of this study would be to expand our understanding of the role of the chemical properties and structure of these molecules in the fluid environment, in relation to the degradation of PA-11.

Lower concentrations could also be used in order to match those of the earlier degradation study for an expanded comparison.
References


http://www.nktflexibles.com/en/Products+and+Solutions/Materials+and+Profiles.html


Acknowledgements

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