

The Effect of Salt Splash on Nylon 6,6

by

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Abstract: One of the most common environmental exposures that nylon undergoes, when used for automotive applications, is that of salt splash, which commonly occurs during winter driving. This study looks at the effect of various salts (NaCl, KCl, CaCl₂) on the thermal and mechanical properties of nylon when exposed to one and four molar aqueous salt solutions. It was found that the diffusion of salt solutions into nylon 6,6 occurred in a pseudo-Fickian manner. Also, it was found that the presence of salt had an effect on the rate of decrease of yield stress with increasing exposure time. The presence of residual salt was found to accelerated deterioration of nylon 6,6, possibly via hydrolysis. In addition, it was found that residual salt was left after water was removed from the system and that this salt was removable.

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Chapter I

Introduction

Nylon 6,6 or poly(hexamethyleneadipamide) is a semicrystalline thermoplastic that was developed in 1938 by Carothers, while working for E.I Dupont. The structure of Nylon 6,6 can be seen in Figure 1.

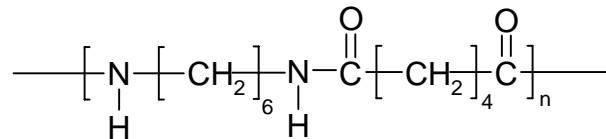


Figure 1 Nylon 6,6

From the time of its discovery until the present, nylon 6,6 has rapidly grown in its prominence and ever increasing number of uses. At present, approximately 50% of the nylon 6,6 resin produced in the United States is used in the automotive industry¹. Unreinforced nylon 6,6 is typically used for hose and wire restrainers, dipstick caps, and liners for sheathed cables. Glass reinforced nylon 6,6 is commonly used for things such as brake fluid reservoirs, and fuel tubing. Nylon 6,6 is also commonly reinforced or blended with other materials in order to produce exterior body components for automobiles¹.

Nylon undergoes a wide variety of environmental exposures when used for automotive applications, but one of the most common is that of salt splash, which occurs during winter driving. It is because of this common use of nylon in the automotive

industry and the frequent exposure to road salts that I chose to study the effect of these salts on nylon 6,6. The salts we chose to study were NaCl, KCl, and CaCl₂. Of the three salts chosen NaCl and CaCl₂ are typically used as road salts, while KCl was chosen as a model compound so as to have two salt cations in the same group of the periodic chart and two in the same period.

In this study we looked at the effects of salt water exposure on a variety of the physical properties of nylon, such as the amount of moisture absorbed and mechanical properties. It is hoped that by better understanding the effects salt exposure has on nylon that any negative effects may be prevented.

The effect of water on nylon 6,6 has been studied in the past and has been found to plasticize nylon. It has been shown that nylon 6,6, which is 57% crystalline, typically absorbs about 7.2 mass percent water², which is less than the maximum amount of 8.5%³, that can be absorbed by nylon 6,6 at room temperature. Once absorbed by the nylon, water can act as a plasticizer. For example, Starkweather has shown that the tensile modulus of dry nylon 6,6 is cut by more than a factor of three, falling from about 4.8 GPa for the dry material to about 1.4 GPa once it is saturated with water⁴. Also, it has been shown that the plasticization of nylon by water causes the stress at yield to drop from approximately 96 MPa when dry to approximately 48 MPa when saturated with water⁵. Finally, the flexural modulus has been shown to drop from about 2.6 GPa to about 0.5 GPa upon saturation with water⁶.

Other experiments performed by Ikeda and Starkweather on an oriented nylon 6,6 tape also show how water plasticizes nylon. They found that for nylon 6,6 tape, in the

machine direction, the modulus dropped from 3.16 GPa for the dry tape to approximately 1.78 GPa for tape saturated with water. Also, they found that the T_g lowered from approximately 120°C for dry nylon to almost 0°C for saturated nylon, which further demonstrates the plasticization of nylon by water⁷.

In addition to the absorption of water, the absorption of dissolved salt has been found to affect the properties of nylon. For example, it has been shown that when nylon is exposed to a salt solution and then dried, there is a gain in mass (Table 1).

Table 1⁸ Residual Salt Mass Increase

| Salt | Concentration | Mass Increase (%) |
|------|---------------|-------------------|
| LiCl | 15M | 0.3 |
| NaBr | 11.3M | 11.3 |
| NaI | 12.3M | 2.29 |
| KI | 7.7M | 12.69 |

The researchers then studied the effect of this residual salt on the ratio of the loss modulus to the storage modulus, or the tan delta, of the nylon, as found using dielectric measurements. They found that there was an increase in the tan delta above 50°C and a decrease in tan delta between 50°C and -120°C, as compared to a control. The magnitude of the increase or decrease in the tan delta was directly related to the amount of salt retained⁸. Further studies of the effects of residual salt on the properties of polymers was performed by Siegmann and Zipora, who looked at the effect of residual

salts on the T_g of nylon 6. In their studies, they exposed nylon 6 films (Figure 2) to saturated solutions of CuCl_2 , FeCl_3 , CuBr_2 , and KCl .

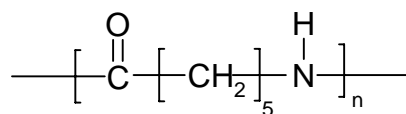


Figure 2 Nylon 6

They found that in a KCl solution nylon did not absorb salt to a significant amount and thus the T_g was not affected, while the other salts were found to significantly affect the T_g of the nylon (Figure 3).

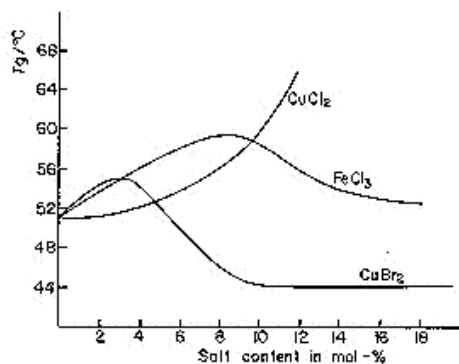


Figure 3 Effect of Salts on T_g ⁹

Siegmann's explanation of this effect is that the absorbed salts complex with the amide groups thus stiffening the chains and increasing T_g , but at the same time this complexing also interferes with hydrogen bonding thus making the chain more flexible and

decreasing T_g . The resulting effect that we see is then a combination of these two competing forces⁹.

In addition to affecting the T_g of nylon 6, residual salt has also been found to affect the IR absorption spectrum and mechanical properties. For example, More and Donald studied the effect of residual $ZnCl_2$, $CaCl_2$, and $NaCl$ on nylon 6. For their experiments they exposed nylon 6 films to 6M salt solutions for 6 hours and then dried them to remove all water. Their work showed that after exposure to $ZnCl_2$ or $CaCl_2$ the transmission IR spectrum of the nylon showed the formation of a new peak at 1600 cm^{-1} . Also, they found that the amide bands at 1540 cm^{-1} and 1635 cm^{-1} were slightly shifted up after salt exposure. It was felt that these changes were reflective of the salts complexing with the amide portion of the polymer. The nylon film exposed to $NaCl$ was found to have no change in its IR spectrum. In addition to the changes in IR absorption it was also found that the residual salt effected the modulus of the polymer (Table 2).

Table 2¹⁰ Modulus After Salt Exposure

| Treatment | Modulus (GPa) |
|-----------|---------------|
| Untreated | 1.84 |
| NaCl | 1.63 |
| $CaCl_2$ | 1.98 |
| $ZnCl_2$ | 2.04 |

The increase in modulus after exposure to either CaCl_2 or ZnCl_2 was thought to be due to a stiffening of the polymer chains as a result of the complexation of the salt with the amide groups. For the case of NaCl , it was felt that the salt only plasticized the polymer since IR data showed that it did not complex with the polymer, therefore lowering the modulus. Further exploration of mechanically tested samples using TEM found that with all of the salts there was a shift from shear deformation to crazing. The crazing in samples exposed to ZnCl_2 or CaCl_2 was thought to be due to deterioration of the chains via chain scission, leading to embrittlement. However, in the case of NaCl the salt leads to plasticization, which results in disentanglement crazing¹⁰.

A second study on the effect of residual salts on the properties of nylon 6 and nylon 6,6 was also performed by More and Donald¹¹. In this study they again looked at the effect of residual NaCl , ZnCl_2 , and CaCl_2 on the mechanisms of deformation, but this time in both nylon 6 and nylon 6,6. They found that in both cases, unsalted films in tension deformed by a combination of true and fibrillated shear. Whenever ZnCl_2 or CaCl_2 was added, there was a switch from shear deformation to crazing, which they believe was a result of chain stiffening by the salt. This stiffening in turn caused a decrease in the amount of shear and chain disentanglement occurring. In the case of NaCl there was still some crazing induced but much less than by the other two salts. Also, they found that CaCl_2 and ZnCl_2 significantly embrittled nylon 6, while the embrittlement was less for nylon 6,6. Since the molecular weight of the nylon 6 was 18,000 and the molecular weight of the nylon 6,6 was 48,000 they believed that the difference in embrittlement effects was due to the differences in chain length. The third salt, NaCl ,

was found not to embrittle either of the nylons, which is a reflection of its lack of interaction with the polymer¹¹.

Dunn and Sansom¹² looked at the effect of exposure to salt solutions on the IR spectrum of nylon 6. They divided the salts tested into two groups depending on their effect. Type I salts included $ZnCl_2$, $FeCl_3$, and $CuCl_2$. These salts all resulted in the formation of a new absorption at 1595 cm^{-1} also the amide I absorption band is shifted to a lower frequency while the amide II absorption band shifts to a higher frequency. Type II salts included $CaCl_2$, $LiCl$, and $MgCl_2$. These salts all resulted in the broadening of the absorption at 3300 cm^{-1} and only small shifts in the amid band absorptions. These differences in the effects of the salt on the IR spectra in turn reflect differences in how the salt complexes with the polymer. The ways in which Dunn and Sansom proposed the salts complex with nylon are seen in Figure 4 and Figure 5, where M^+ is the salt cation.

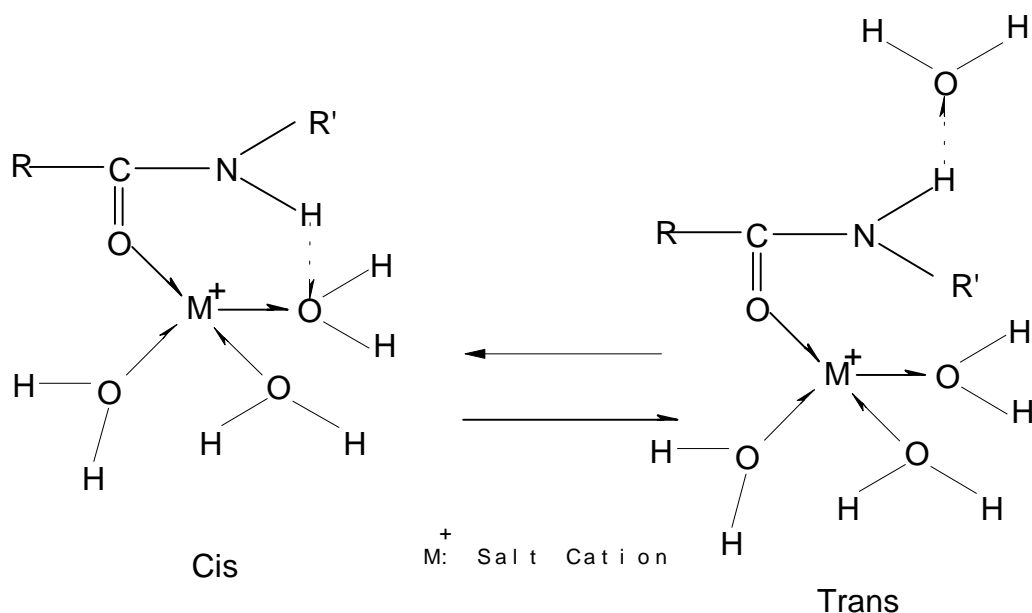


Figure 4 Interaction With a Type I Salt¹²

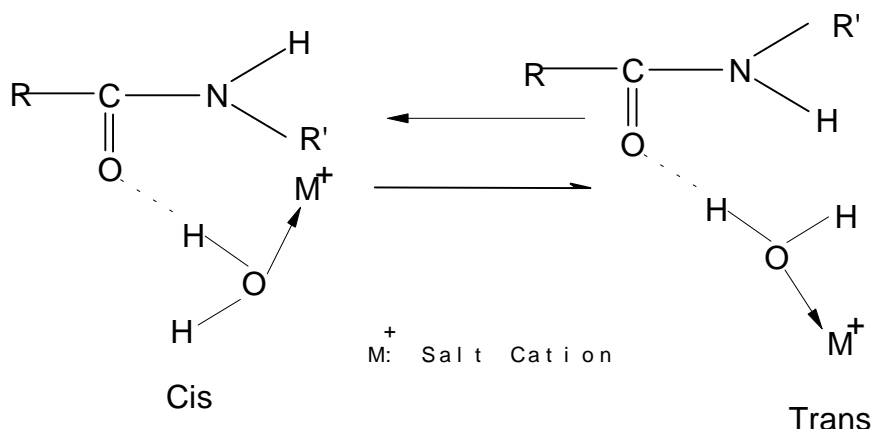


Figure 5 Interaction With a Type II Salt¹²

In Figure 4 there is coordination between the carbonyl and the metal, which results in the formation of the new peak at 1595 cm^{-1} . Also, in Figure 4 there is a transformation from the trans form to the cis form. In the cis form the amid bands are closer than in the trans form, thus explaining the observed shift of the two bands toward one another. In Figure 5 we see the proposed structure for the interaction with type II salts. Here we see that the nitrogen is no longer involved in hydrogen bonding, which allows for free stretching of the N-H bond, thus broadening the peak at 3300 cm^{-1} ¹².

Another study that looked at the effect of salt and salt solutions on nylon was performed by Wyzgoski and Novak. In their work they, in particular, looked at the effect of NaCl and CaCl₂ on nylon 6,6 and nylon 6. They found that the temperature had a significant effect on the amount of salt solution absorbed. For example, when nylon 6,6 was exposed to a 6.7 M solution of CaCl₂ at 50°C it absorbed about 3% by mass at equilibrium. When the temperature was increased to 75°C the moisture picked up increased to approximately 12%. Finally when the temperature was increased to 100°C

the amount absorbed increased to about 28%. They also studied the effect of salt concentration on the amount of moisture absorbed. Their results showed that at 100°C nylon 6,6 in water absorbed about 8.6% by mass. If instead of water the nylon was exposed to a 3M solution of NaCl at 100°C the amount of moisture absorbed dropped to 6%. Finally if nylon is exposed to a 6.1M NaCl solution at 100°C the amount of moisture absorbed dropped further to about 4.5%.

Wyzgoski and Novak studied the partitioning of CaCl₂ and water in the film using atomic absorption spectroscopy, their results for a 6.7M solution can be seen in Table 3.

Table 3¹³ Salt/Water Partitioning at Various Temperatures

| Temp (°C) | Mass Increase (%) | Composition (wt%) | | | Concentration in film (M) |
|--------------|-------------------|-------------------|-------------------|------------------|------------------------------|
| | | Ca | CaCl ₂ | H ₂ O | |
| 50 | 3.0 | 0.2 | 0.6 | 2.4 | 2.4 |
| 75 | 22.0 | 2.3 | 6.3 | 11.7 | 4.9 |
| 100 | 28.5 | 3.1 | 8.5 | 13.8 | 5.6 |

These data show that as the temperature of the salt solution increases and correspondingly the amount of moisture absorbed increases the salt concentration in the film approaches that of the salt solution concentration. This data indicates that in a CaCl₂ solution, nylon 6,6 does not absorb water and salt at the same rate, but rather absorbs more water than salt, thus resulting in a lower salt concentration in the film than in the salt solution. Also, it appears that for CaCl₂, as the temperature increases, the rate of

absorption for salt increases much more rapidly than it does for water, thus increasing the concentration of the salt solution in the film. However, in these experiments the concentration of salt solution in the nylon never reaches that of the original solution. Their results for nylon in a variety of salts at 100°C can be seen in Table 4.

Table 4 Salt/Water Partitioning With Various Salts

| Salt | Concentration (M) | Mass Increase (%) | Composition (wt%) | | | Concentration in film (M) |
|-------------------|----------------------|-------------------|-------------------|------|------------------|------------------------------|
| | | | Cation | Salt | H ₂ O | |
| CaCl ₂ | 6.7 | 28.5 | 3.1 | 8.5 | 13.8 | 5.6 |
| LiCl | 15.0 | 25.9 | 0.6 | 3.4 | 17.1 | 4.7 |
| MgCl ₂ | 5.7 | 23.8 | 1.1 | 4.4 | 14.8 | 3.1 |
| NaCl | 6.1 | 4.6 | 0 | 0 | 4.6 | 0 |
| H ₂ O | - | 8.5 | 0 | 0 | 8.5 | 0 |

Their data show that, unlike the other salts, NaCl does not absorb into the nylon film, thus they conclude that it can have no effect. Also, it appears that the salts with a 2+ charge are absorbed more readily than those with a 1+ charge. This of course results in the concentration of salt solution in the film being closer to the actual salt solution concentration.

Wyzgoski and Novak also looked at the effect of exposure to a 6.7 M CaCl₂ solution at 100°C on the molecular weight of nylon 6,6 (Table 5).

Table 5 Deterioration of Molecular Weight

| Time in solution | M_n ($\times 10^4$) | M_w ($\times 10^4$) | M_z ($\times 10^4$) |
|------------------|-------------------------|-------------------------|-------------------------|
| 0 | 4.3 | 14.4 | 4.78 |
| 4 Days | 4.32 | 14.5 | 4.67 |
| 30 Days | 3.96 | 12.3 | 3.99 |

The fact that there is no change in the molecular weight after 4 days of exposure tends to imply that there is no degradation of the polymer chains at this stage. Degradation does not appear to occur until longer periods of time, as shown by the decrease in molecular weight at the 30 day period.

When looking at IR spectra, Wyzgoski and Novak found that absorbed CaCl_2 interacted with the amide portion of the polymer. They found that the absorbance corresponding to N-H, C=O, and C-N were all shifted down and broadened, suggesting a change in the chemical environment of the amid. DSC studies of the effect of CaCl_2 and water on the melting behavior of nylon 6,6 showed that nylon, which had been equilibrated with CaCl_2 at 100°C , had a more complex recrystallization and melting behavior than dry nylon. This suggests that the salt and water increases recrystallization of the nylon. After the water is removed by the first heating and the sample is quenched, it was found that the nylon was totally amorphous, suggesting residual salt alone acts to inhibit crystallization. Crystallinity studies using the DSC were also performed on samples that had been saturated by CaCl_2 and then saturated with water to remove all

salts. These studies showed that this process resulted in no changes in the crystallinity of the samples.

The effect of saturation at 100°C with CaCl₂ on the tan δ of nylon 6,6 was also studied using dynamic mechanical analysis. This work showed that saturation with water and salt increased the apex of the T_g peak from 83°C, for dry nylon 6,6, to 130°C for saturated nylon. If the water is removed via heating, we find that the apex of the T_g peak increases to 190°C. This implies that salt acts to restrict chain motion thus increasing T_g. Studies of the mechanical behavior showed that residual CaCl₂ decreased the modulus from 2.03 GPa to 0.83 GPa. Also, the tensile strength of the nylon 6,6 slightly decreased from 108.1 MPa to 101.9 MPa. Finally the elongation at break was found to increase from 125% to 178%. This data tends to imply that the residual CaCl₂ plasticizes the nylon, thus lowering the T_g which, of course, is in direct opposition to the dynamic mechanical data. The authors gave no good explanation of how these two results could be reconciled.¹³

It has been shown that one of the effects of having water present in nylon 6,6 is that the polymer chain can undergo hydrolysis, resulting in chain scission. The scheme for this reaction can be seen in Figure 6.

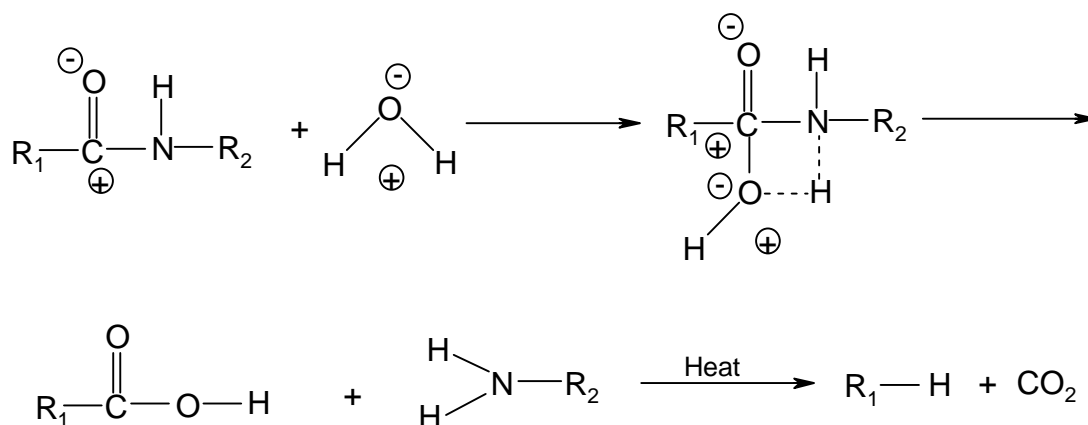


Figure 6 Hydrolysis of Nylon¹⁴

In this reaction nylon is attacked by water, resulting in the formation of carboxylic acid chain end and an amine chain end. The chain ending with the carboxylic acid can then undergo a decarboxilation resulting in the release of CO₂.

In chapter 2, we will outline the experimental procedures used in this research. In chapter 3 we will discuss the results of the individual experiments performed. Finally, in chapter 4 we will combine the individual results to arrive at our final conclusions, and in chapter 5 we will look at some potential future work.

Chapter II

Experimental

2.1 Materials

The materials used in this work are listed alphabetically below.

Calcium Chloride Dihydrate, Aldrich Chemical Company, was used as obtained.

Polyhexamethylene Adipamide, E. I. Dupont, Dartek C-101, in the form of a 0.1 mm thick film, was used as obtained.

Potassium Chloride, Aldrich Chemical Company, was used as obtained.

Sodium Chloride, Mallinckrodt Chemical Company, was used as obtained.

Deionized Water, Obtained from the tap via a Barnstead/Thermolyne filtration system

2.2 Procedures

2.2.1 Pre-Treatment

All nylon films when received were subjected to a pretreatment that consisted of an initial heating to 100°C, in a Fisher Isotemp[®] Vacuum Oven, for twenty-four hours in order to remove any residual monomer or other small molecules left in the film from the manufacturing process.

2.2.2 Preparation of Salt Solutions

Salt solutions were prepared by stirring the appropriate amount of salt, weighed on a 0.01g Mettler PM300 Balance, in the correct amount of deionized water, on a

stirring hot plate until the salt was dissolved. Prior to use, all salt solutions were allowed to equilibrate to room temperature.

2.2.3 Moisture absorption

The amount of water absorbed by the nylon is determined by taking a piece of nylon film that has been prepared as specified in 2.2.1. The initial mass of this film, measured using a +/- 0.1 mg Mettler AE50 balance, is recorded, after which the film is submerged in the appropriate solution. After five minutes of submersion, the film is removed from the solution. Upon removal, all surface moisture is removed via paper towel, and the sample is weighed. After weighing, the film is resubmerged in its solution. This process was repeated every five minutes until the masses obtained become constant, after which the time between weighings is increased to ten minutes. The interval between weighings increased as was required until the sample has reached a total submersion time of twenty-four hours. During long term exposures, over one hour, the container holding the salt solution is stored in a 1 gallon Ziploc[®] storage bag so as to avoid the molarity increasing due to evaporation. This process was repeated five times and averaged in order to obtain absorption curves.

2.2.4 Yield Stress

In order to study the changes in the yield stress of the nylon as a result of exposure to the salt solutions, dog bone specimens (23 mm X 7.88 mm) are cut using a manual DGD Expulsion Press from Dewes-Gumbs Die Co. The specimens are cut from films prepared as described in 2.2.1 and exposed to salt solutions for varying amounts of time before being removed. Upon removal from the salt solution, surface moisture was

removed via paper towel. The samples were tested using a Texture Technologies TA-XT2I Texture Analyzer with a 5 Kg load cell at a deformation rate of 0.1 mm/sec until failure. The yield stress was chosen to be the point at which elastic deformation ended and plastic deformation began (Figure 7). This test was performed on five samples at each exposure time and averaged.

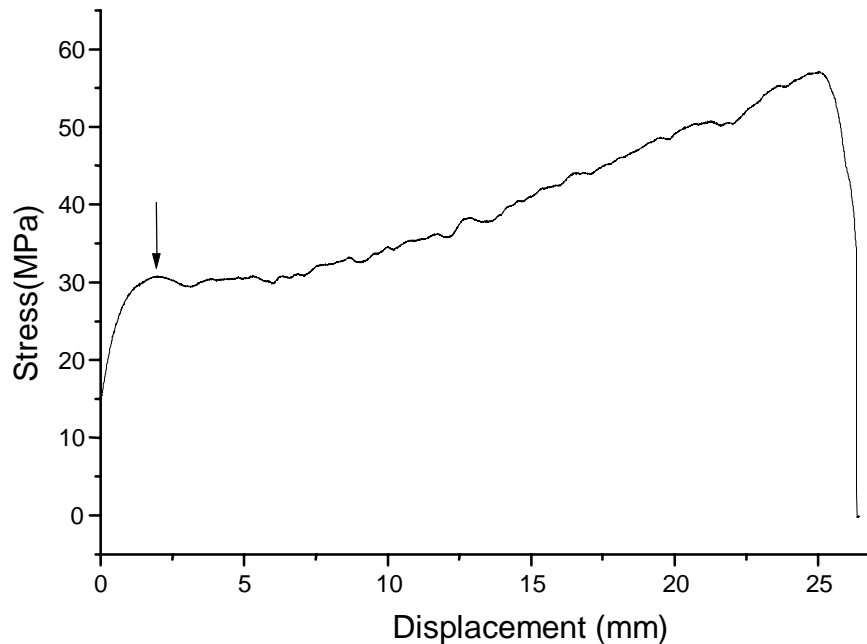


Figure 7 Determining Yield Point

2.2.5 Residual Salt Content and Reversibility of Salt Absorption

The amount of salt absorbed by the films and the reversibility of the salt absorption was studied by first heating a sample of nylon film to 100°C for twenty-four hours to remove all absorbed water. After drying, the film is weighed and then submerged in the appropriate salt solution for twenty-four hours. After soaking in the

salt solution the film is removed, surface moisture is removed with a paper towel, and the sample is weighed. After weighing, the nylon film is once again placed in the oven at 100°C for twenty-four hours to remove all absorbed water, leaving the salt behind. After drying, the nylon is once again weighed to find the amount of residual salt contained in the film. Once the amount of residual salt is determined, the nylon film is then submerged in fresh water for twenty-four hours in order to remove as much of the residual salt as possible. After being removed from the water the sample is again dried at 100°C for 24 hours. After drying the film is weighed, so as to determine how much of the residual salt is removed.

2.2.6 Determination of Film Crystallinity

In order to determine the amount of crystallinity in the nylon 6,6 films, samples were heated from 25°C to 300°C at a rate of 20°C per minute using a Perkin Elmer Pyris 1 Differential Scanning Calorimeter. From the DSC scan the ΔH of melting was found using the data analysis function in the Pyris software. In order to determine a crystallinity index, the ΔH of melting was divided by the theoretical heat of fusion for nylon 6,6, which is 46.5 KJ/mole¹⁵.

2.2.7 UV/Vis Spectroscopy

During this research it was found that film left in the oven for an extended period of time yellowed. This yellowing was thought to be due to deterioration of the film. In assessing the amount of deterioration taking place in the films upon heating, the ultraviolet / visible spectrum of the films was monitored. This was done using an Ocean Optics S2000 Fiber Optic Spectrometer with a LS-1 tungsten halogen lamp. All samples to be tested were first soaked in their respective solutions for 24 hours, after which they

were placed in an oven at 100°C. The samples were removed from their oven for testing after time periods of 5 and 7 days. All results were reported as relative absorbencies, which were normalized to their baseline between 177.13 nm and 250.02 nm.

2.2.8 Differential Scanning Calorimetry

In order to look at the melting and recrystallization behavior of nylon 6,6, samples were heated from 20°C to 300°C at a rate of 10°C per minute using a Perkin Elmer Pyris 1 Differential Scanning Calorimeter. Samples that had been saturated with a salt solution, dried in an oven at 100°C for 24 hours, and left on the bench for 24 hours to equilibrate to ambient conditions, were scanned twice using the DSC. Also, some identically prepared samples were placed in an oven at 300°C for 10 minutes and then quenched in liquid nitrogen in order to see how the salt would effect the recrystallization of the sample.

2.2.9 Infrared Spectroscopy

Infrared spectra were taken on a Perkin Elmer model 1600 FT-IR spectrophotometer. Prior to taking spectra, all nylon 6,6 samples were saturated with a salt solution and then left to dry in an oven at 100°C for 24 hours. Attempts were made to obtain spectra using both reflectance and transmission modes.

Chapter III

Discussion of Results

3.1 Pre-Treatment

The effect of the pre-treatment was to permanently remove a small amount of mass from the sample as can be seen in Figure 8. Upon heating, the mass of the nylon 6,6 film drops to about 96.63% of its initial value. After cooling and equilibrating to room conditions, the lost moisture is regained thus increasing the mass to 99.75% of its original value, representing a loss of 0.25% of the samples original mass. If the sample is cooled and equilibrated two more times, we find that after each equilibration the sample mass returns to the 99.75% level. This indicates that with the initial heating there is a permanent loss of mass, which we believe to be due to the evaporation of small molecule species such as additives or residual monomer.

3.2 Film Crystallinity

From DSC studies we determined that the as received nylon 6,6 film is approximately 34.6% crystalline. However, after pre-treating a sample and saturating it with water and drying it in the oven, it was found that the crystallinity increased to 37.5%, which we believe was due to additional cold crystallization in the oven. Also, if instead of exposing a sample to fresh water we expose it to a 1M KCl solution and then dry it, we find that the crystallinity is 37.6%, showing negligible change from the sample exposed to water. This indicates that KCl does not effect the ultimate degree of crystallinity of the nylon.

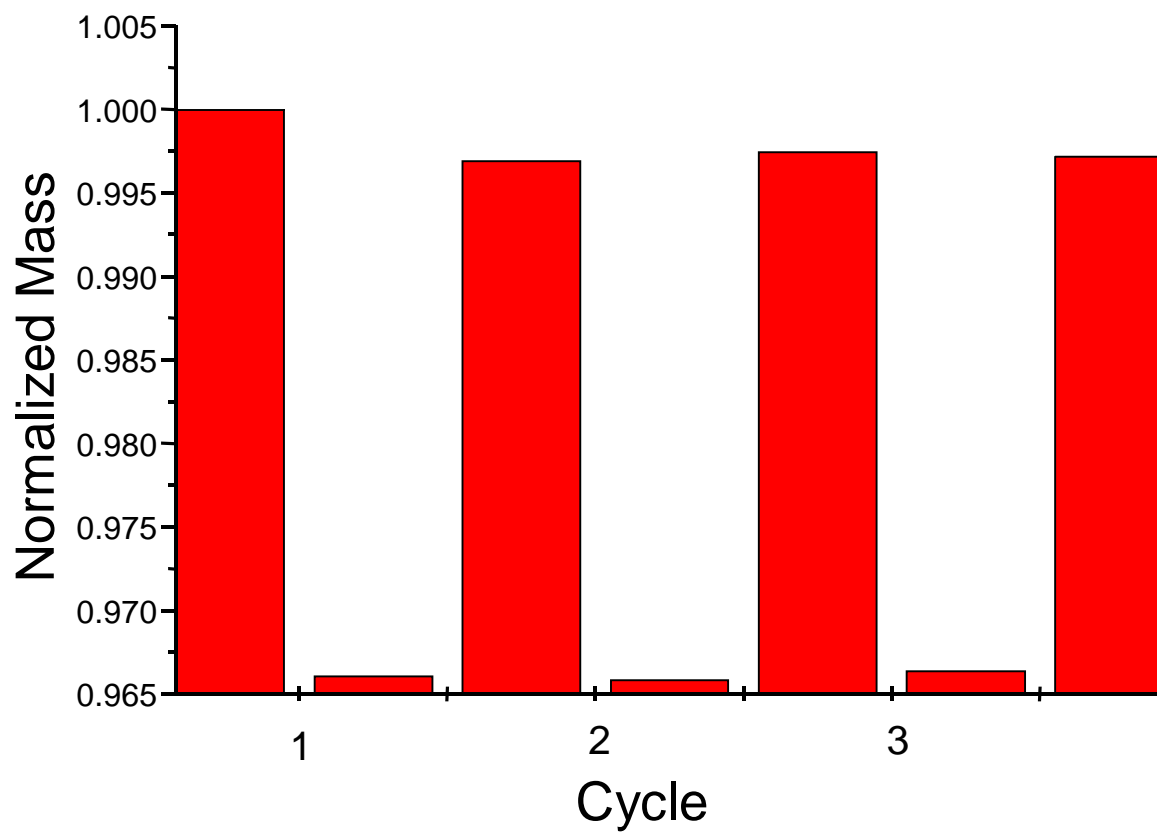


Figure 8 Mass Loss Upon Initial Heating

3.3 Moisture Absorption

The amount of moisture absorbed by the nylon 6,6 films was measured using the technique described in section 2.3.3. The amount of moisture absorbed by the films over time when exposed to one molar (1M) and four molar (4M) salt solutions can be seen in Figure 9 and Figure 10, respectively. As can be seen from Figure 9, when the nylon 6,6 is exposed to our control, water, the film at equilibrium absorbs between 5 and 6 mass percent of moisture. However, when a sample of nylon film is exposed to a 1M Potassium Chloride (KCl) salt solution, the amount of moisture absorbed at equilibrium by the film increases to between 7.5 and 8 mass percent. If instead of a 1M KCl solution we expose a sample of the nylon 6,6 film to a 1M Calcium Chloride (CaCl_2) solution, we find that at equilibrium the amount of moisture absorbed decreases to approximately 6.5 mass percent. Finally, if a film sample is exposed to a 1M Sodium Chloride (NaCl) solution, then the amount of moisture absorbed at equilibrium falls to between 5 and 5.5 mass percent.

If instead of exposing nylon 6,6 film samples to a 1M salt solution we expose them to 4M solutions, we find the amount of moisture absorbed by the film decreases (Figure 10). For instance, when a nylon film sample is exposed to a 4M KCl solution we find that at equilibrium the amount of moisture absorbed is between 5.5 and 6 mass percent. This represents a decrease of about 2 mass percent from a 1M KCl solution. When we expose a sample of nylon film to a 4M NaCl solution we find that at

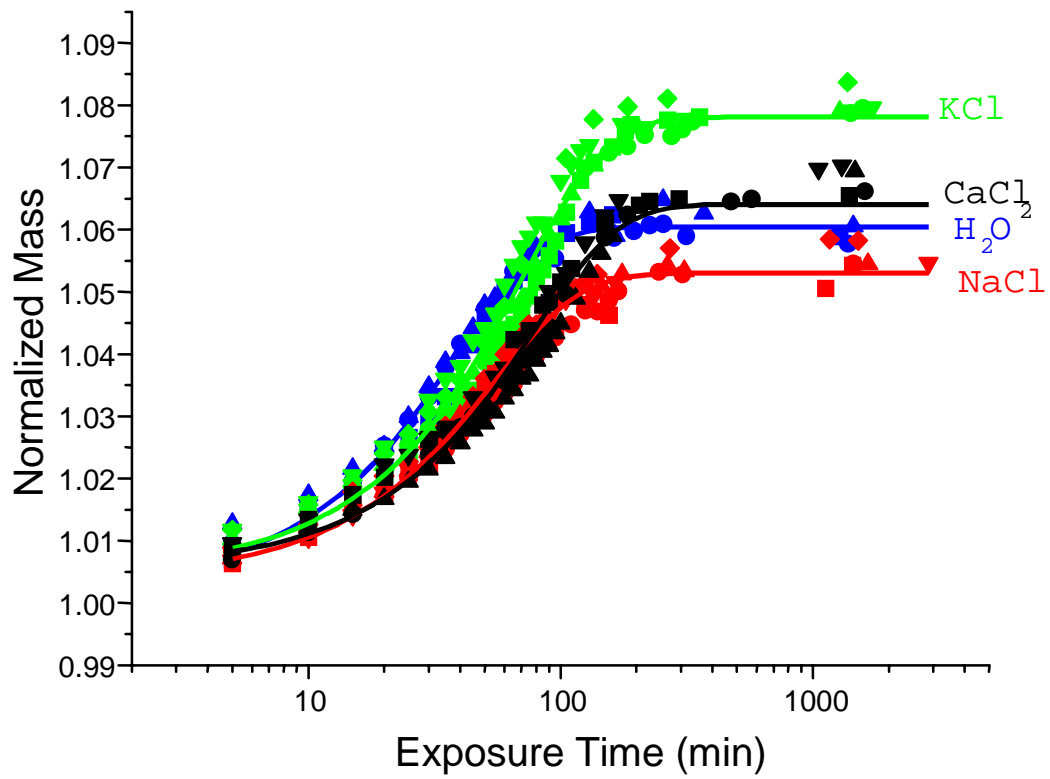


Figure 9 Absorption of 1M Salts

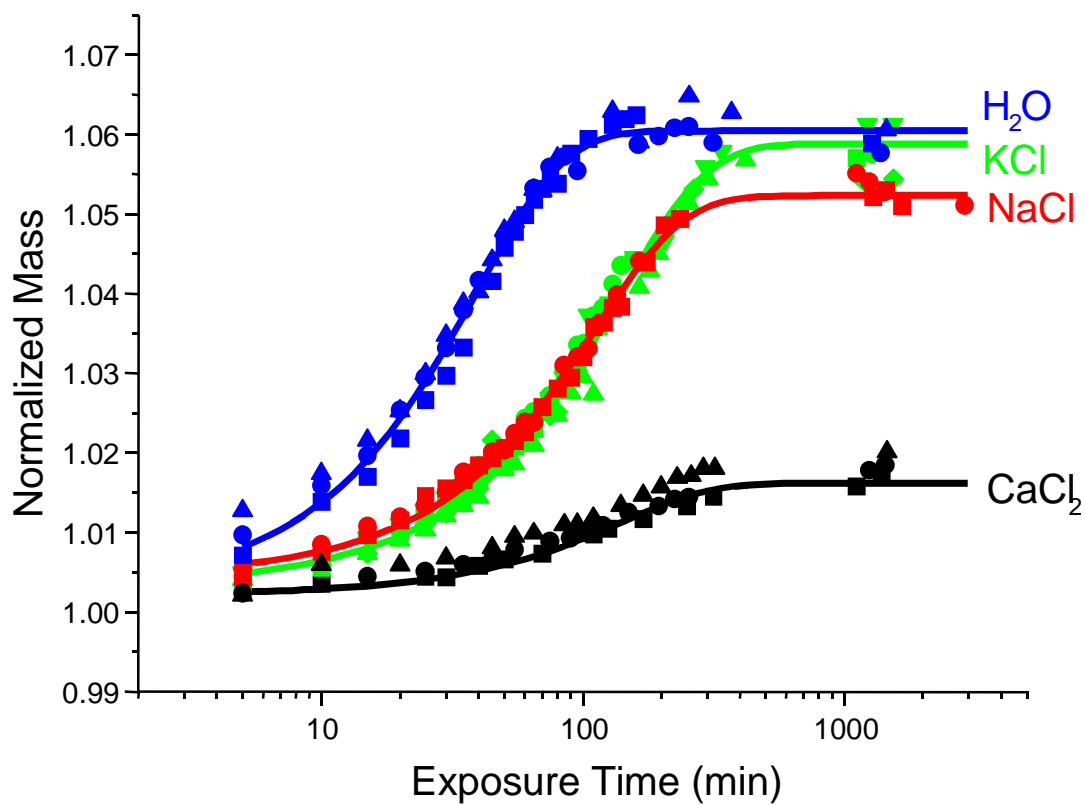


Figure 10 Absorption of 4M Salts

equilibrium the film absorbs between 5 and 5.5 mass percent, which represents no real change from the amount absorbed when exposed to a 1M NaCl solution. Finally, if we look at the moisture absorbed at equilibrium by a nylon 6,6 film when exposed to a 4M CaCl₂ solution we find that it significantly decreases, as compared to when exposed to a 1M CaCl₂, to approximately 1.75 mass percent. All of the above moisture absorption data is summarized in Table 6 below.

Table 6 Moisture Absorbed

| Solution | Concentration | Equilibrium Mass Percent Increase | Standard Dev. |
|-------------------|---------------|--------------------------------------|---------------|
| H ₂ O | N/A | 5.90 | 0.14 |
| KCl | 1M | 7.87 | 0.04 |
| CaCl ₂ | 1M | 6.78 | 0.23 |
| NaCl | 1M | 5.45 | 0.01 |
| KCl | 4M | 5.82 | 0.21 |
| NaCl | 4M | 5.17 | 0.11 |
| CaCl ₂ | 4M | 1.86 | 0.14 |

If, instead of graphing normalized mass versus exposure time as in the figures above, we look at the normalized mass versus the square root of time, we find that the absorption curves become linear until saturation (Figure 11 and Figure 12). The linearity of the curves at early absorption times implies that the diffusion taking place is Fickian. In order to calculate the diffusion constants we must first calculate the flux of salt solution in to the film,

$$J = -M \frac{d\mu}{dx} \quad (1)^{16}$$

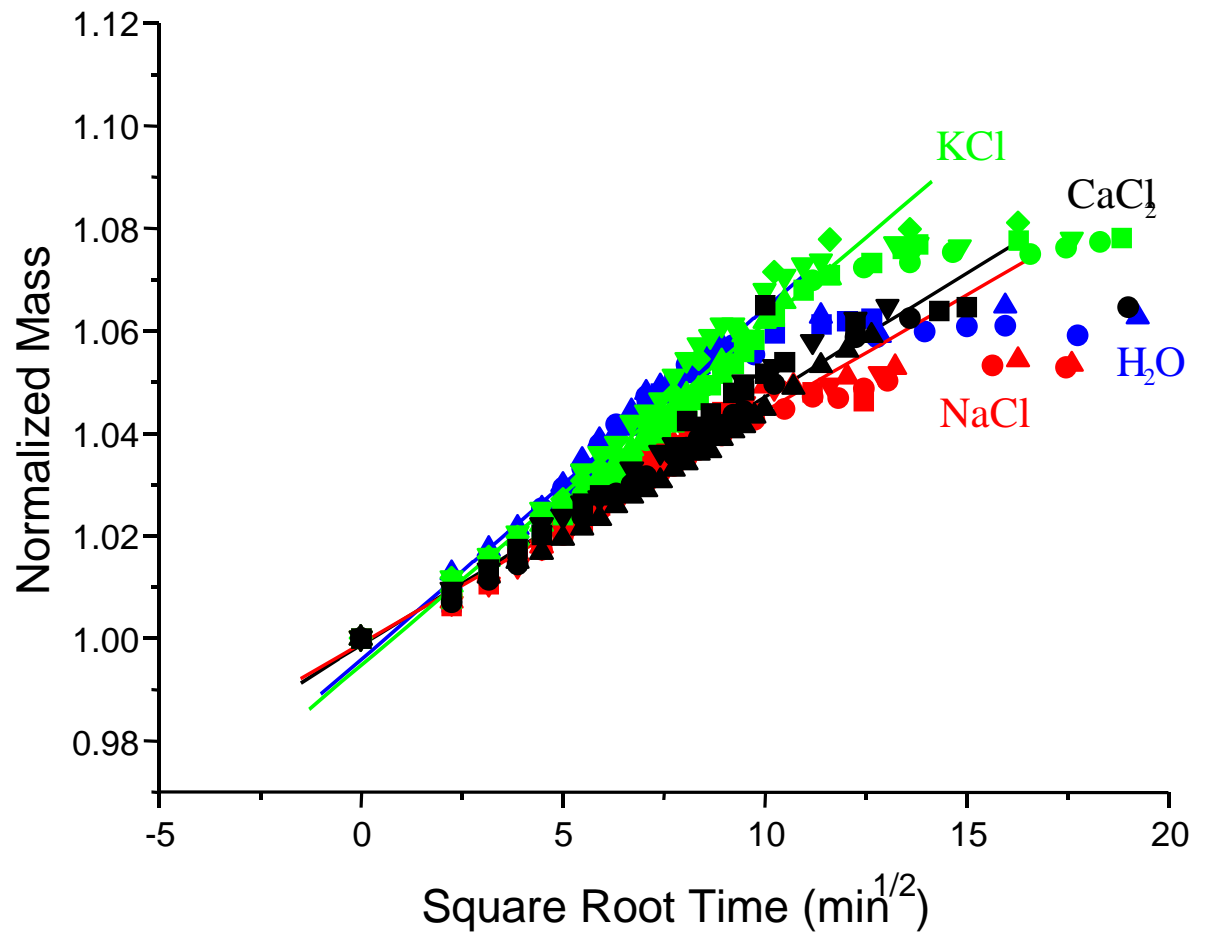


Figure 11 Fickian Absorption of 1M Salt Solutions

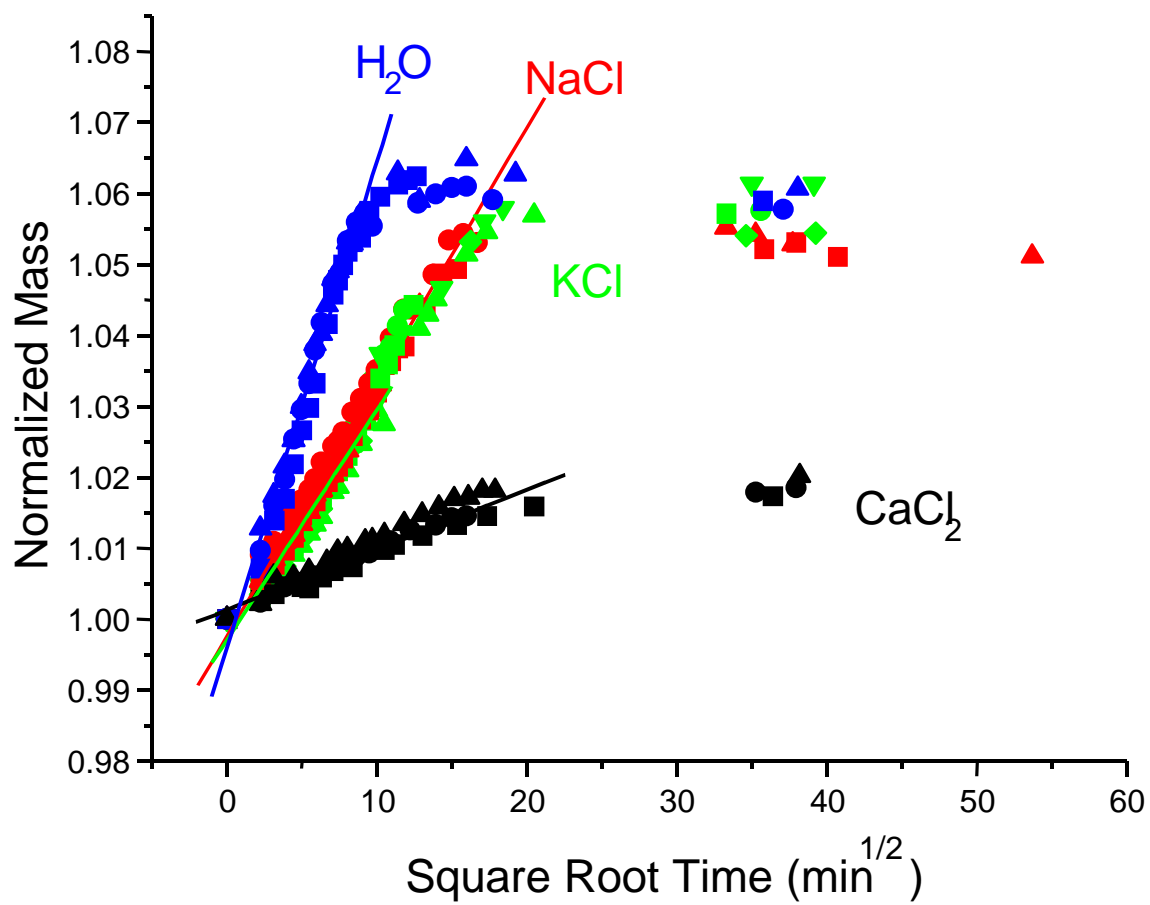


Figure 12 Fickian Absorption of 4M Salts

where J is flux, M is a constant, μ is chemical potential and x is position. If it is assumed that salt solution behaves as an ideal dilute solution then chemical potential is proportional to concentration via Henry's law, resulting in Fick's second law,

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (2)$$

where C is concentration, x is position, t is time and D is the diffusion coefficient. In this process, it is assumed that the diffusion constant D is independent of concentration. If we assume that the diffusion is only through the faces, that the ambient temperature and humidity are constant, that initial material temperature and humidity are uniform, and that the diffusion coefficient is constant, we can rewrite Equation 2 in a new form.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (3)$$

If we then apply boundary conditions and integrate, we can rewrite Equation 3 in its final form, which will allow us to calculate a diffusion coefficient for each system.

$$D = \pi \left(\frac{h}{4M_e} \right)^2 \left(\frac{dM_t}{dt^{1/2}} \right)^2 \quad (4)$$

Here h is the film thickness, M_e is the mass uptake at equilibrium, and $dM_t/dt^{1/2}$ is the slope of the linear portion of Figures 11 and 12.

The resulting diffusion coefficients for each of the salt solutions can be seen in Table 7.

Table 7

Diffusion Coefficients

10^{-12} (cm²/sec)

| Salt | 1M | 4M |
|-------------------|------|-----|
| KCl | 11.0 | 3.3 |
| NaCl | 5.8 | 2.2 |
| CaCl ₂ | 8.3 | 0.3 |
| H ₂ O | 14.3 | |

From Table 7 we see a significant drop in the diffusion coefficients as the salt concentration increases. This means that the diffusion coefficient is not independent of concentration, which invalidates the earlier assumption that lead to Fick's second law. This implies that the chemical potential of the salt is changing with increasing concentration. Since the absorption curves in Figure 11 and 12 are linear, but the diffusion constant is not independent of salt concentration, it can be said that the diffusion taking place is not Fickian, but rather pseudo-Fickian. It is also useful to notice that the diffusion coefficients for all of the salt solutions are less than that for water, even

though the amount of moisture absorbed at equilibrium in some of the salt solutions is larger than for water.

3.4 Yield Stress

The results of the mechanical testing can be seen in Figure 13, 14, 15. From Figure 14 we see that the salt solution that results in the smallest amount of decrease in the yield stress with increasing sample exposure time is 4M CaCl₂, while H₂O results in the greatest decrease in yield stress with increasing exposure time. The rate at which exposure to a solution decreases yield stress is reflected in the slopes of the lines in Figures 13, 14, and 15. Lines with a relatively shallow slope reflect a smaller decrease in yield stress with increasing exposure time while those with a steeper slope reflect a greater decrease in yield stress with increasing exposure time. As mentioned above, exposure to a 4M CaCl₂ solution results in the smallest decrease in yield stress, which is reflected in its shallow slope. Exposure to 4M CaCl₂ is followed, in order of increasing effect on yield stress and increasing slope, by 4M KCl and 4M NaCl, respectively.

Finally, the curves for the exposure to 4M salt solutions is followed by those for exposure to 1M salt solutions. The curves representing exposure to the 1M salt solutions have little difference and appear to be statistically equivalent. All of the salt exposure curves are then followed by the curve representing exposure to water, which has the steepest slope and the greatest effect on yield stress.

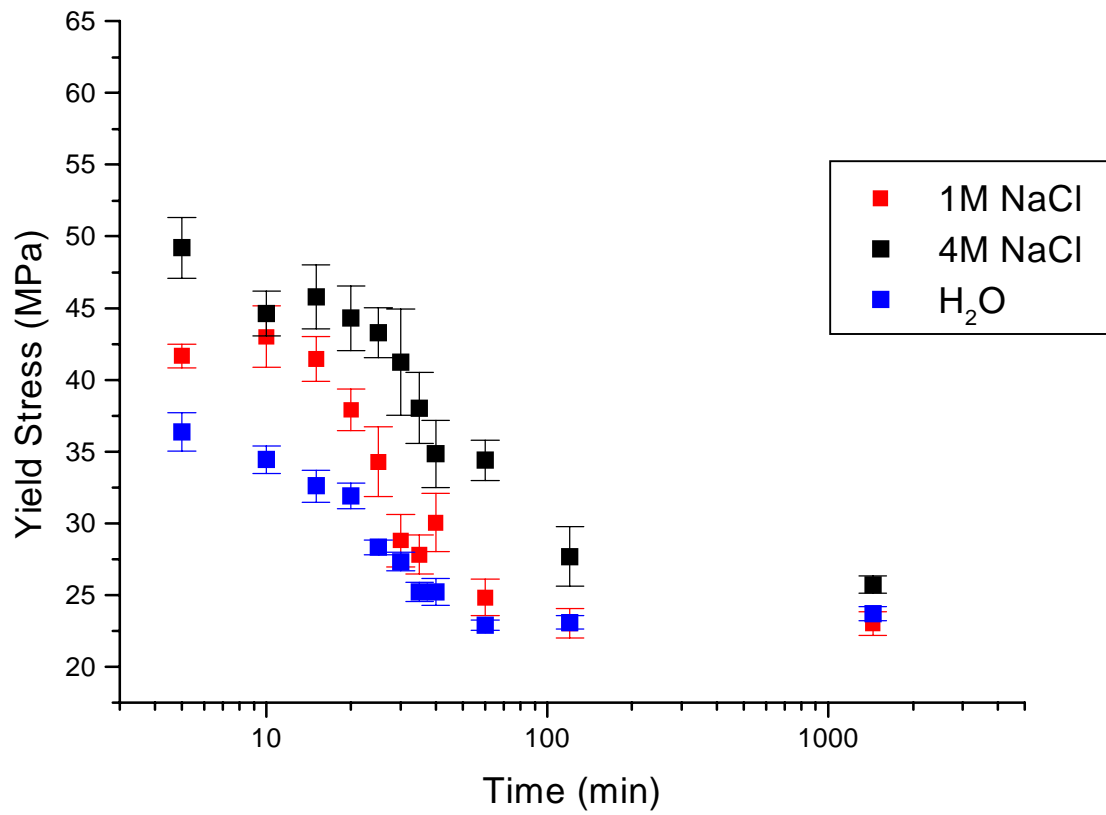


Figure 13 Yield Stress vs Exposure Time For NaCl

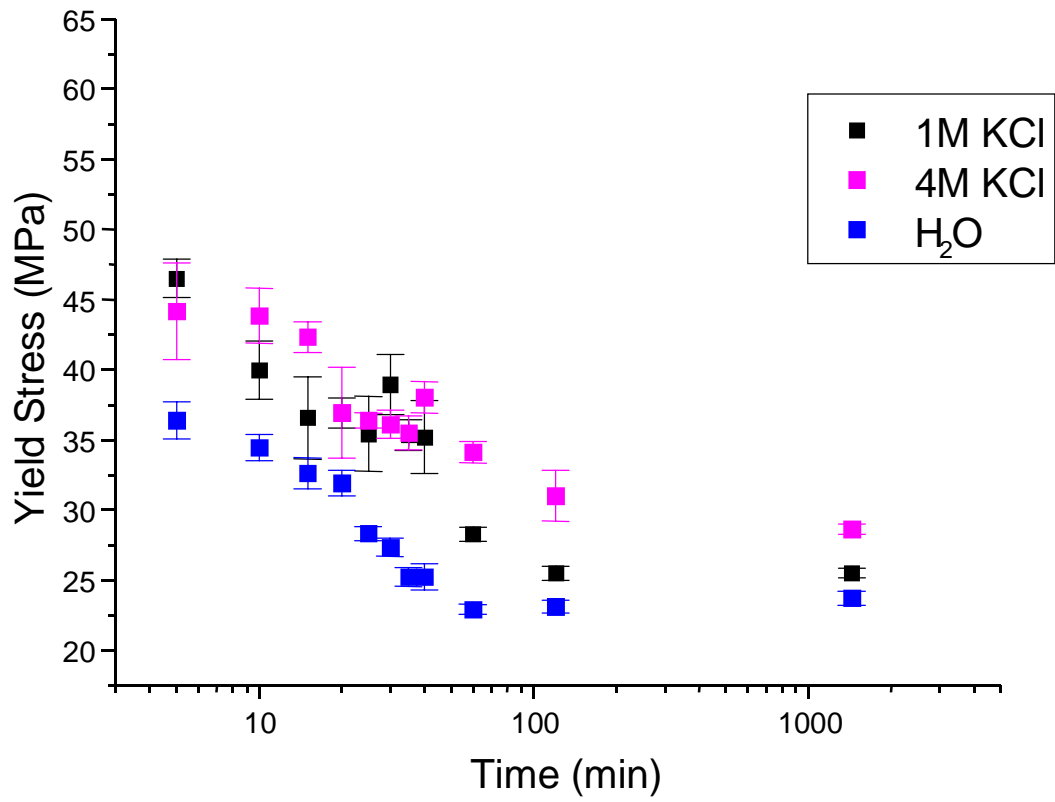


Figure 14 Yield Stress vs Exposure Time For KCl

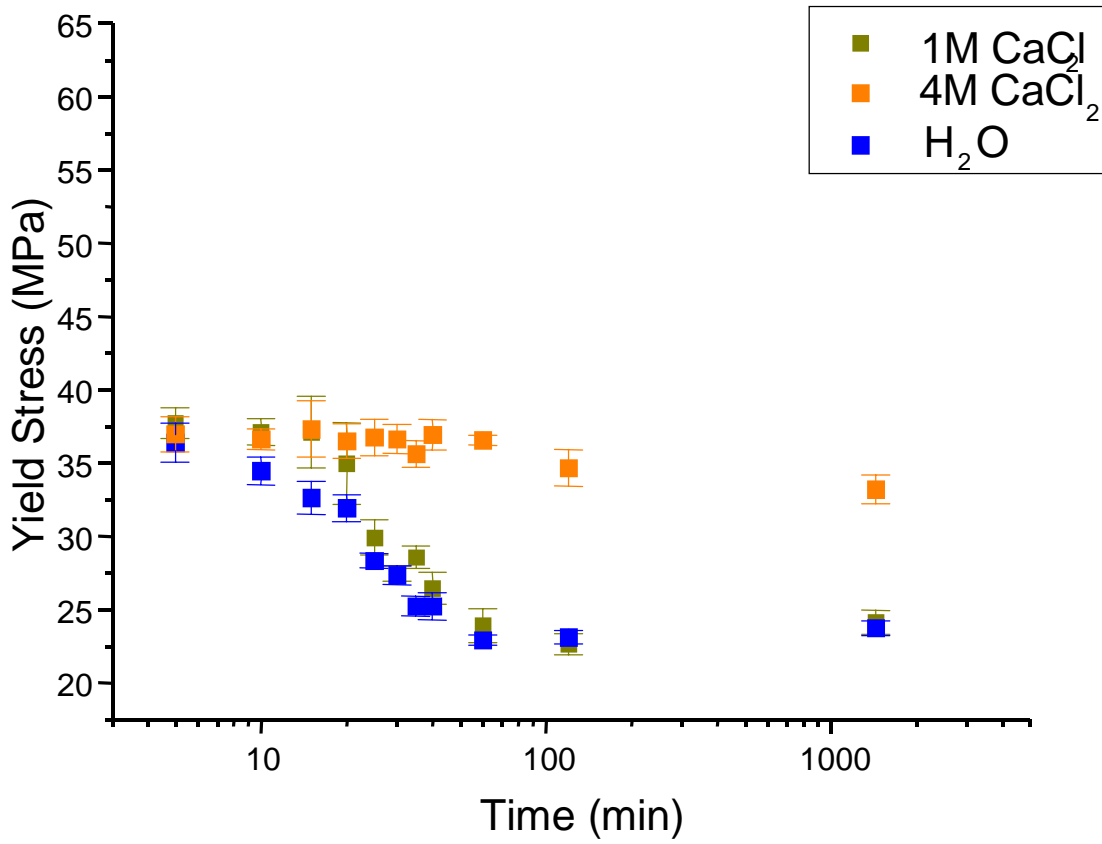


Figure 15 Yield Stress vs Exposure Time For CaCl₂

If the decrease in yield stress that is seen in Figures 13, 14, and 15 is due only to plasticization, then we would expect to see all of the curves fall onto one line if yield stress is plotted versus the amount of water absorbed rather than time. In Figure 16 we have plotted the yield stress versus the percent mass increase of the polymer. As can be seen, all of the data do not fall on the same line but have been compressed into a smaller area. This indicates that there are possibly more forces working to decrease the yield stress than just plasticization.

3.5 Salt Retention

The results of the study to determine the amount of salt retained by the nylon films and the reversibility of the salt retention can be seen in Figure 17. As can be seen, only four of the solutions show an increase in mass after exposure to a salt solution and drying. The other three, H₂O, 1M KCl, and 1M NaCl show a decrease in mass. Finally, after exposure to water and drying, all of the samples show a decrease in mass from the starting mass.

Ideally, the mass of the film that was only exposed to water should have remained constant, at one, for the entire experiment. The fact that it does not indicates that there may be some deterioration of the film occurring during drying. In order to account for this deterioration we can normalize the mass of each sample by dividing by the mass of the sample exposed only to water,

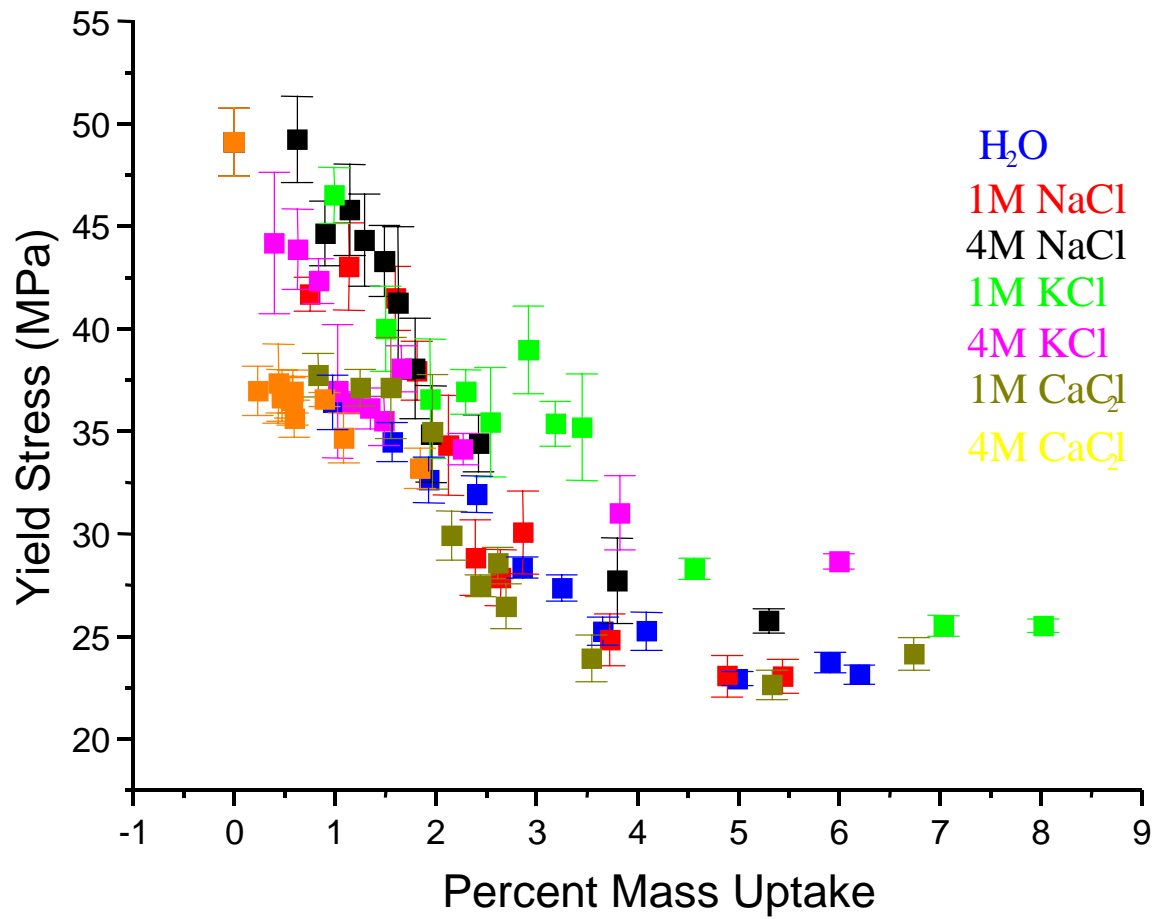


Figure 16 Yield Stress vs Mass Uptake

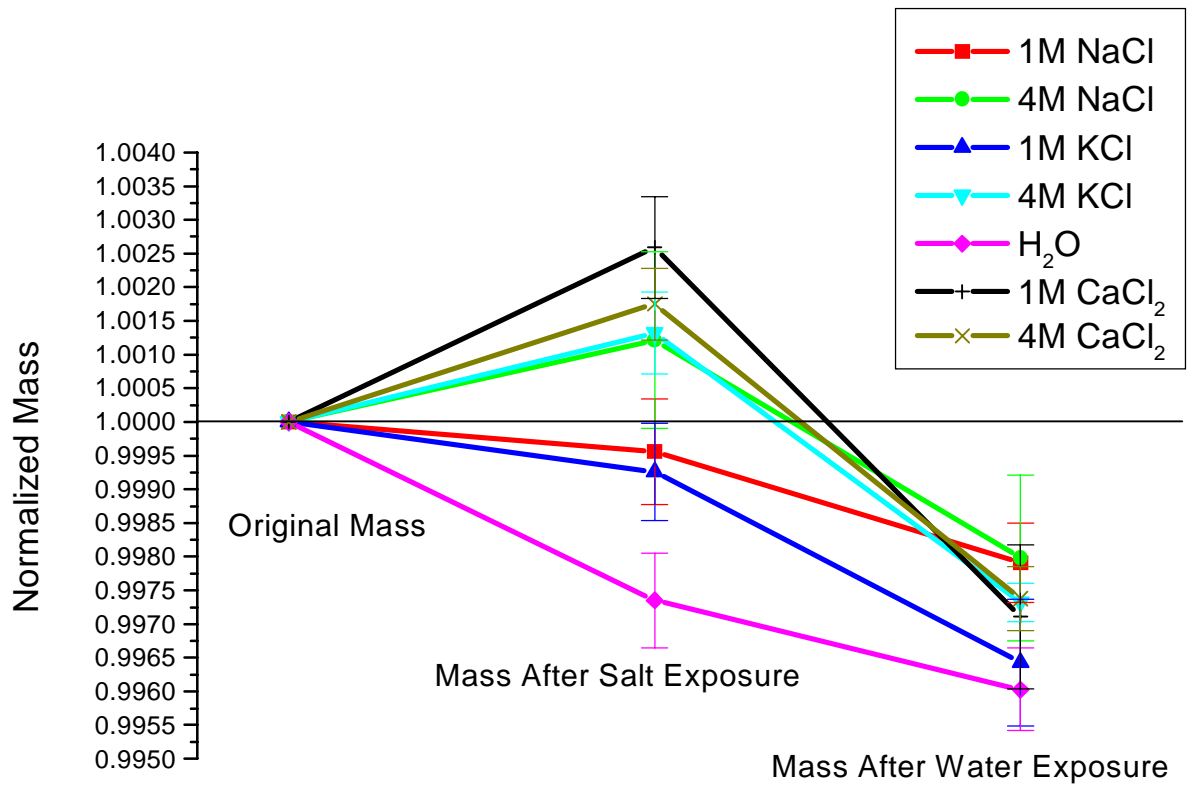


Figure 17 Mass Uptake Due To Residual Salt

thus forcing the water curve to be held constant at one (Figure 18). From this figure we see that when exposed to either the 1M or 4M CaCl_2 solutions, the films gain the most mass, while the film picks up the least mass when exposed to the 1M KCl solution. Samples exposed to the remaining salt solutions are in between the two extremes and are statistically indistinguishable.

The amount of mass gained by the films after exposure to salt solutions is less than would be expected. For example, both the sample exposed to 4M KCl and the one exposed to 4M NaCl pick up about 0.37% mass. If however the amount of moisture absorbed by the film left all of its salt behind, then exposure to the 4M KCl solution should result in an increase of about 1.49%, while exposure to the 4M NaCl solution should result in an increase of about 0.98%. This result could imply that either the moisture absorbed by the film is of a lower salt concentration than the overall solution or that not all salt remains behind when the water is removed. Finally, we see that upon exposure to water and drying that the mass of the samples returns to the original value, within experimental error. This implies that exposure to water removes residual salt from the film.

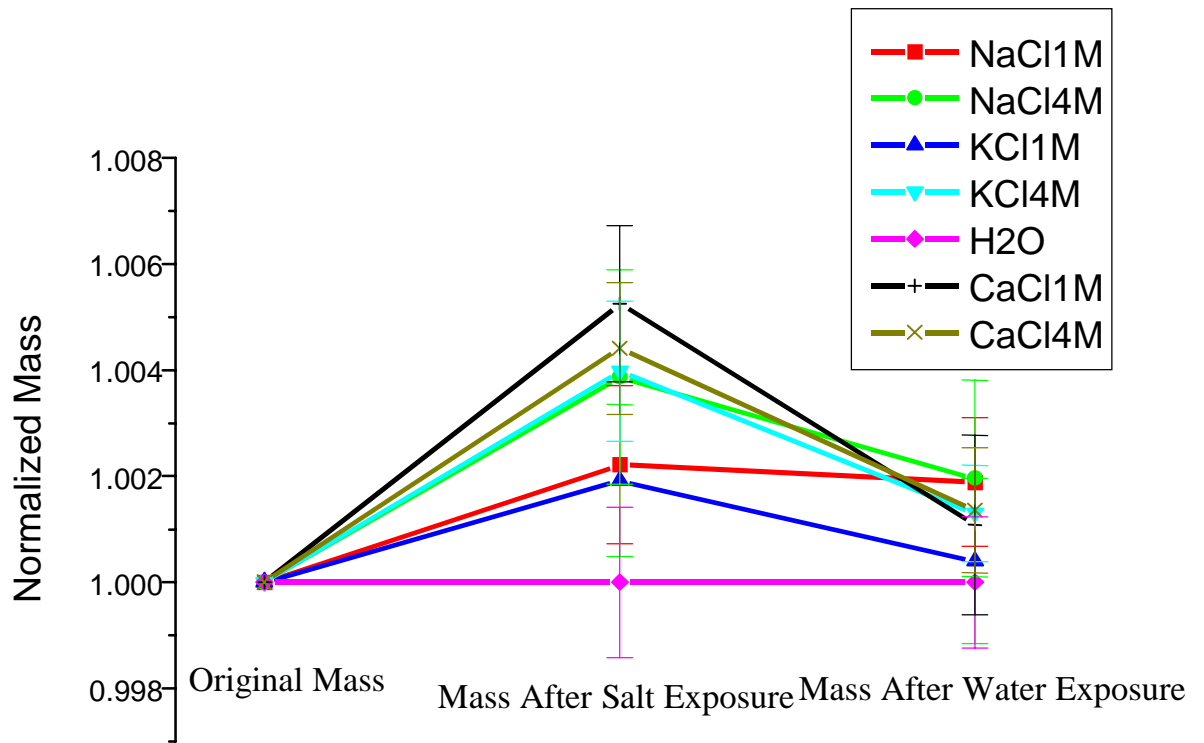


Figure 18 Normalized Mass Uptake Due to Residual Salt

3.6 UV/Vis Spectroscopy

After looking at the UV/Vis spectra for nylon exposed to each salt and at both concentrations, as well as some that were exposed to no salt, we can draw several conclusions. First, it appears that exposure to water alone does not affect the rate of polymer degradation. From Figure 19 we see that while there is an increase in absorbance with increasing time of exposure in the oven, there is no significant difference between the spectrum for a sample that has been saturated with water before being placed in the oven and one that has only been exposed to the oven conditions.

Secondly, it appears that the presence of residual salt accelerates the yellowing of nylon films. In Figures 20, 21, and 22 we see the spectra for nylon samples saturated with NaCl, KCl, or CaCl₂, respectively. After 7 days in the oven, all of the samples reach a maximum relative absorption of between 9.6 and 11.8, which represents a significant decrease in the appearance of the film. However, the samples that were only saturated with water or were exposed to no liquids only reach a maximum absorption of between 4.0 and 4.25 after 7 days in the oven. Furthermore, it appears that of the three salts, CaCl₂ has the strongest accelerating effect on deterioration, while NaCl has the second strongest and KCl has the least. In Figure 23, we see the spectra for samples exposed to each of the salts in the form of a 1M solution. Here, we see that the sample saturated with 1M CaCl₂ and then left in the oven for 7 days has a greater absorbance than samples that had been exposed to NaCl or KCl solutions and left in the oven for 7 days. If we look at samples that have been saturated with 4M salt solutions prior to being placed in

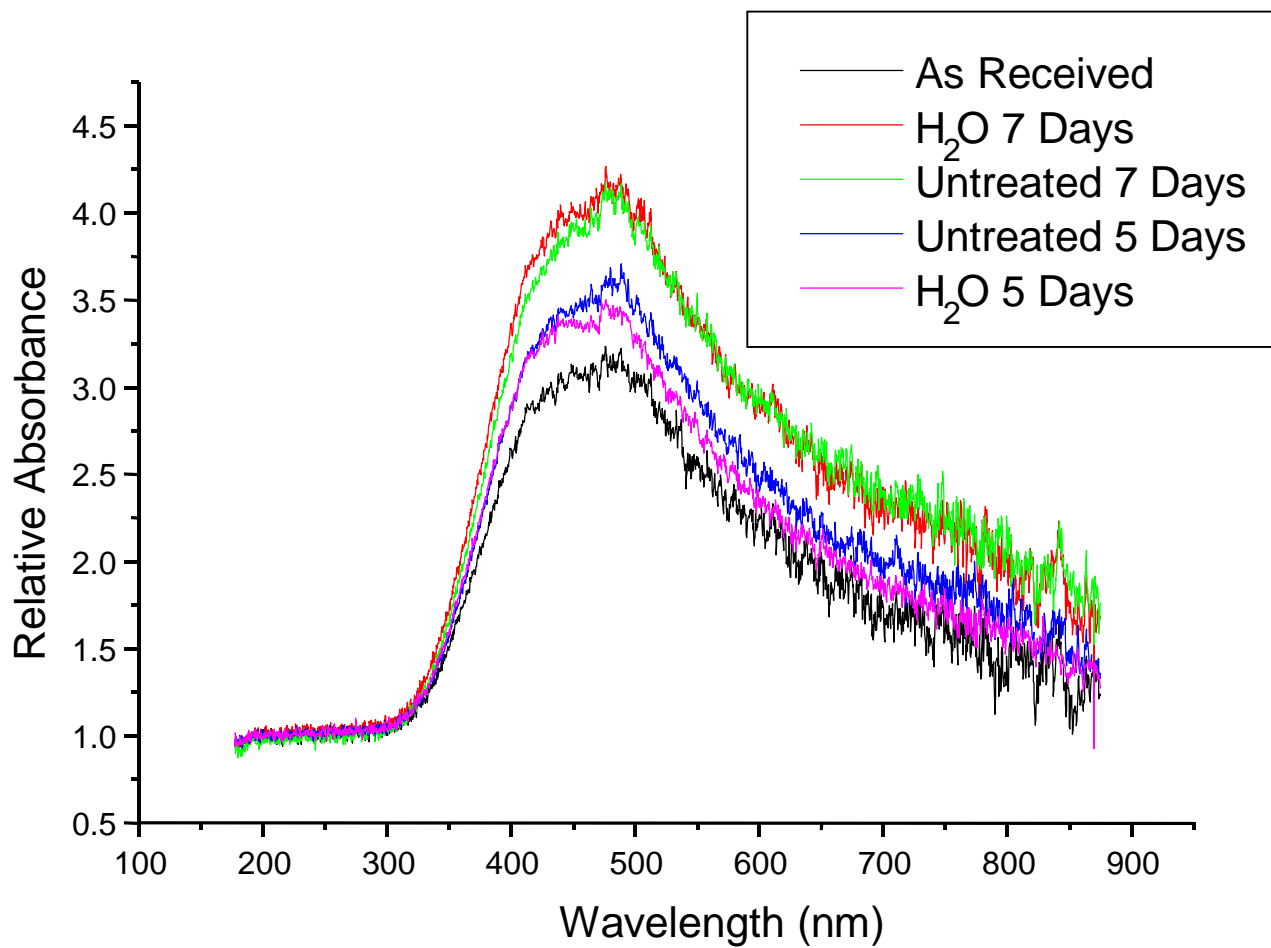


Figure 19 UV/Vis Absorption of Controls

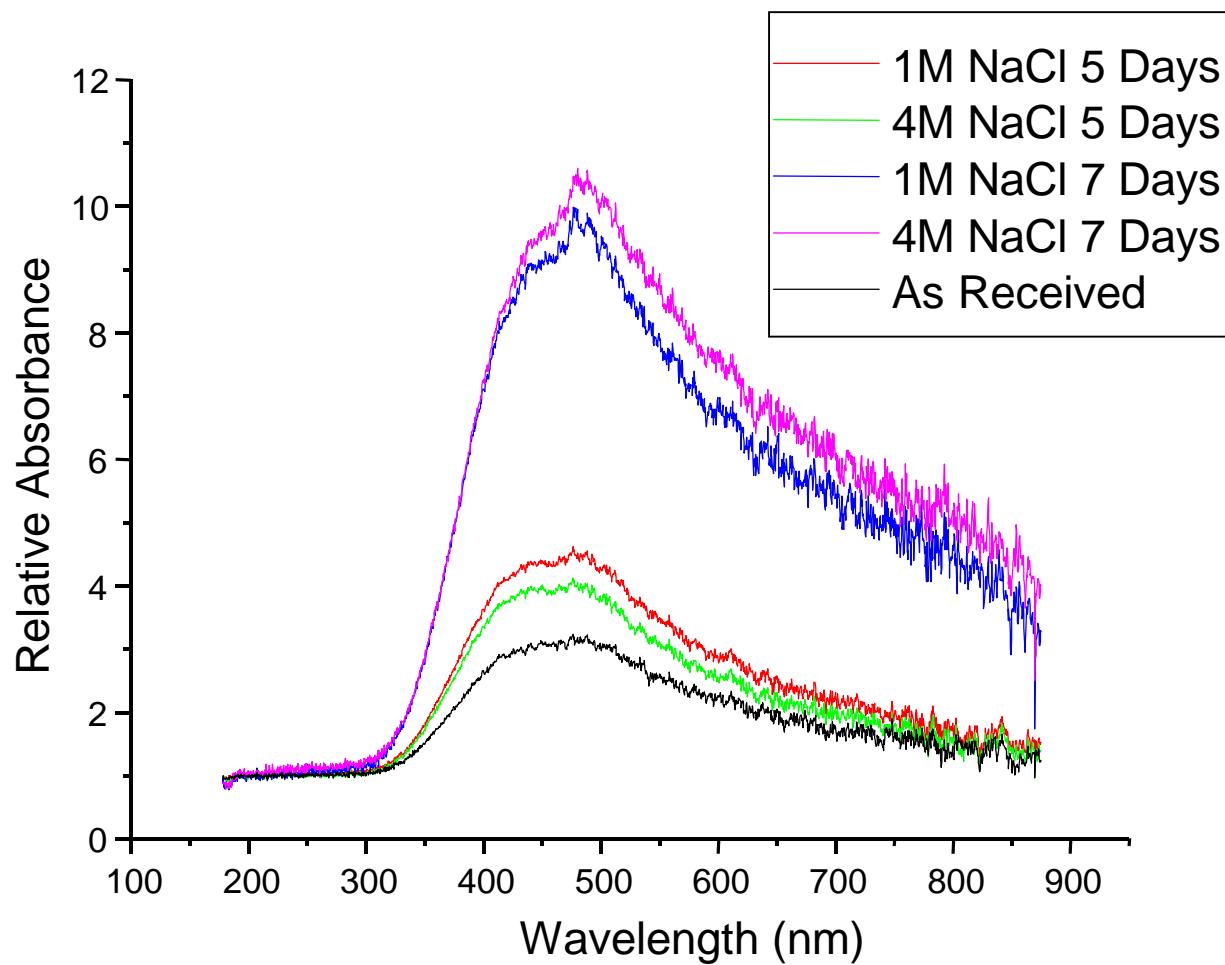


Figure 20 UV/Vis Absorption After Exposure to NaCl

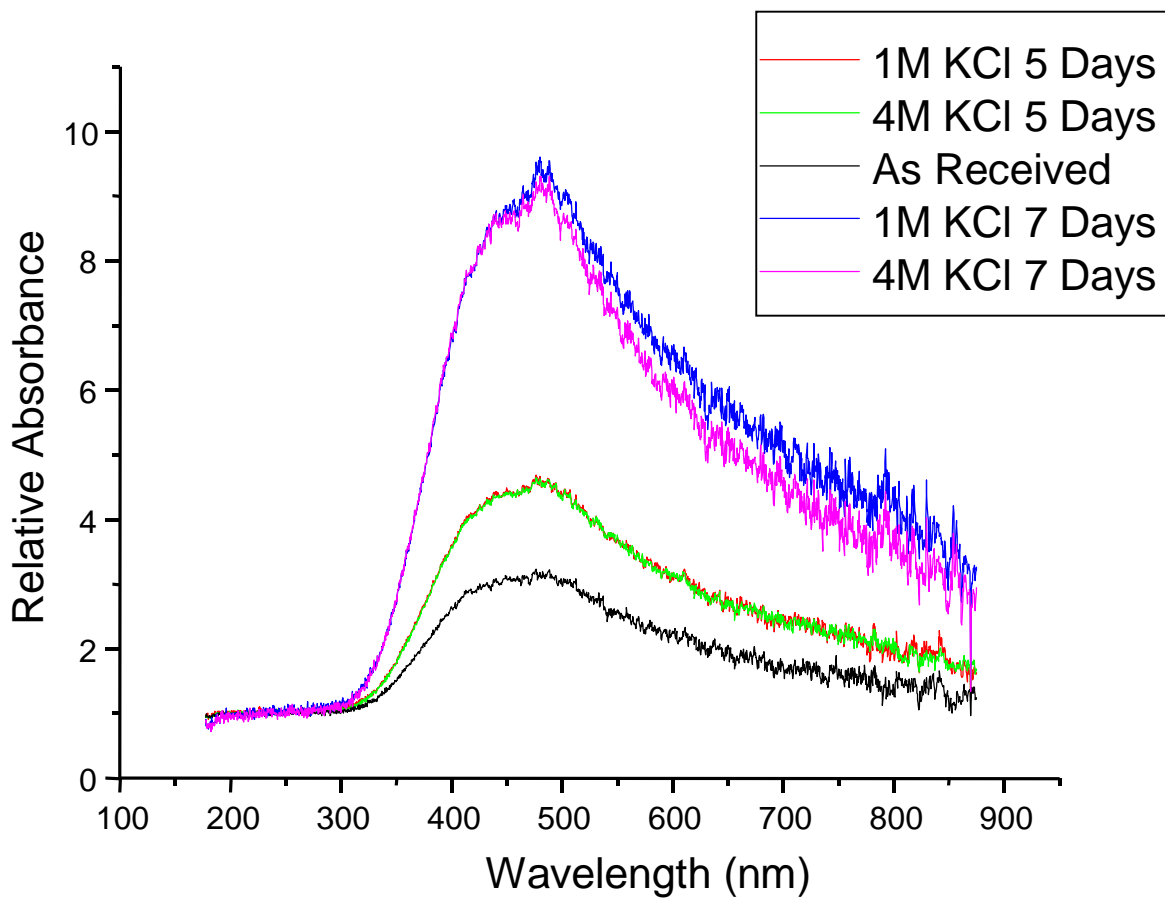


Figure 21 UV/Vis Absorption After Exposure to KCl

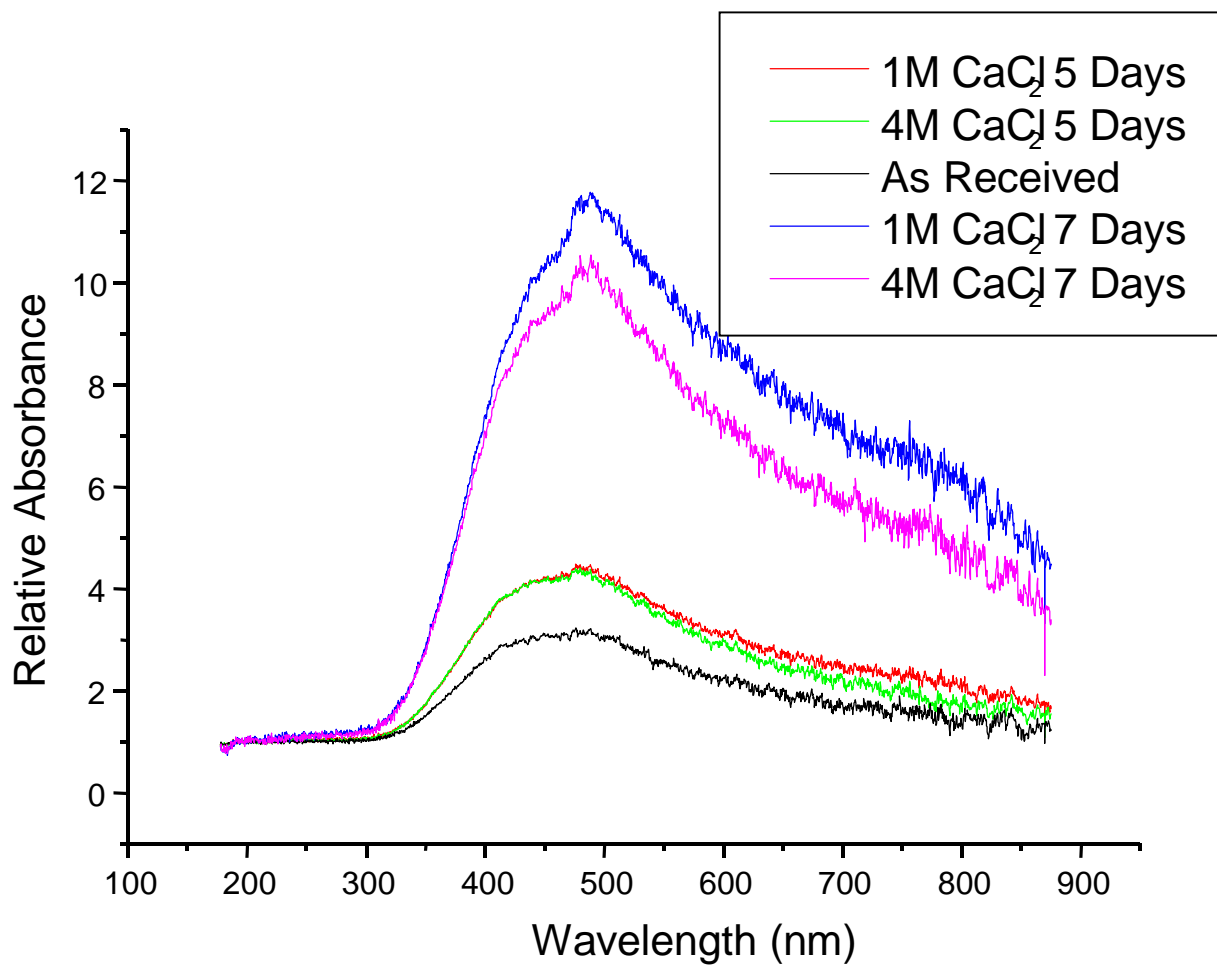


Figure 22 UV/Vis Absorption After Exposure to CaCl₂

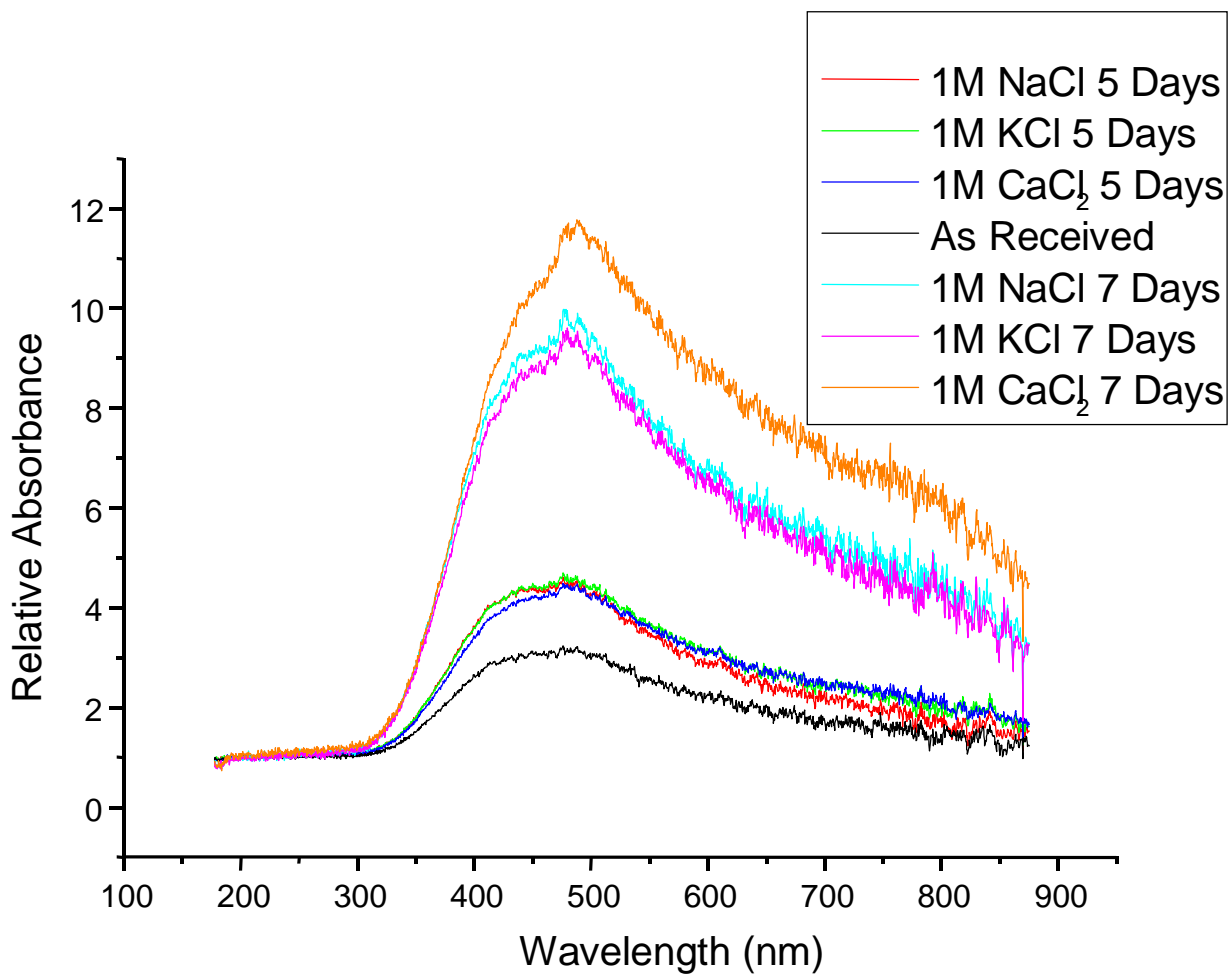


Figure 23 UV/Vis Absorption After Exposure to 1M Salts

the oven for 7 days, we find that those exposed to CaCl_2 and NaCl have the highest absorbencies, while those exposed to KCl have the least (Figure 24). The apparent ability of CaCl_2 to accelerate deterioration may be due to the greater charge of the Ca^{2+} ion as compared to either the K^+ or the Na^+ ion, which allows it to interact more strongly with the polymer chain. In the case of exposure to 4M solutions, the amount of CaCl_2 absorbed by the nylon film is minimal, thereby allowing its effect to be minimized and its deteriorating effect to be equaled by NaCl . The apparent ability of NaCl to accelerate deterioration more than KCl may be due to its smaller size, thus allowing it greater access to the polymer chains. A proposed idea for how the presence of salt could accelerate the degradation process can be seen in Figure 25.

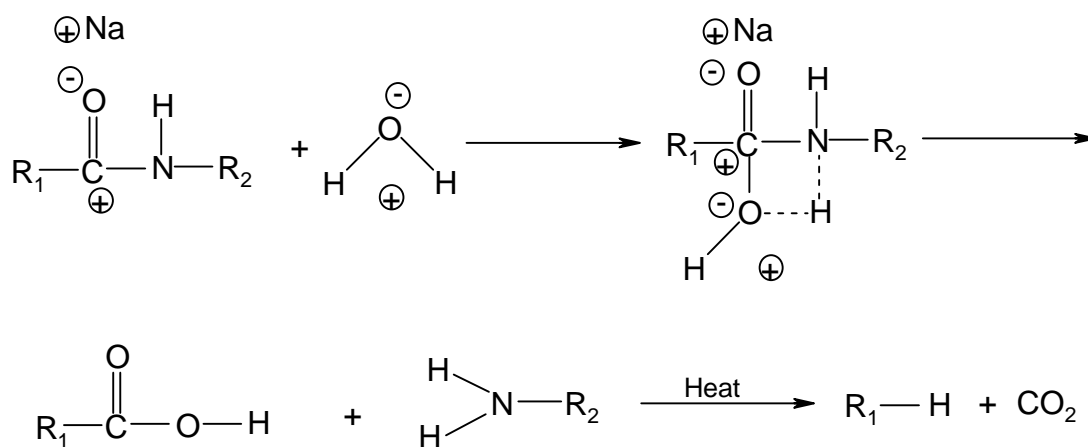


Figure 25 Salts Accelerating Degredation

In this reaction the salt interacts with the carbonyl making it more electron withdrawing, thus making the carbon more susceptible to attack by the water, thus accelerating the entire process.

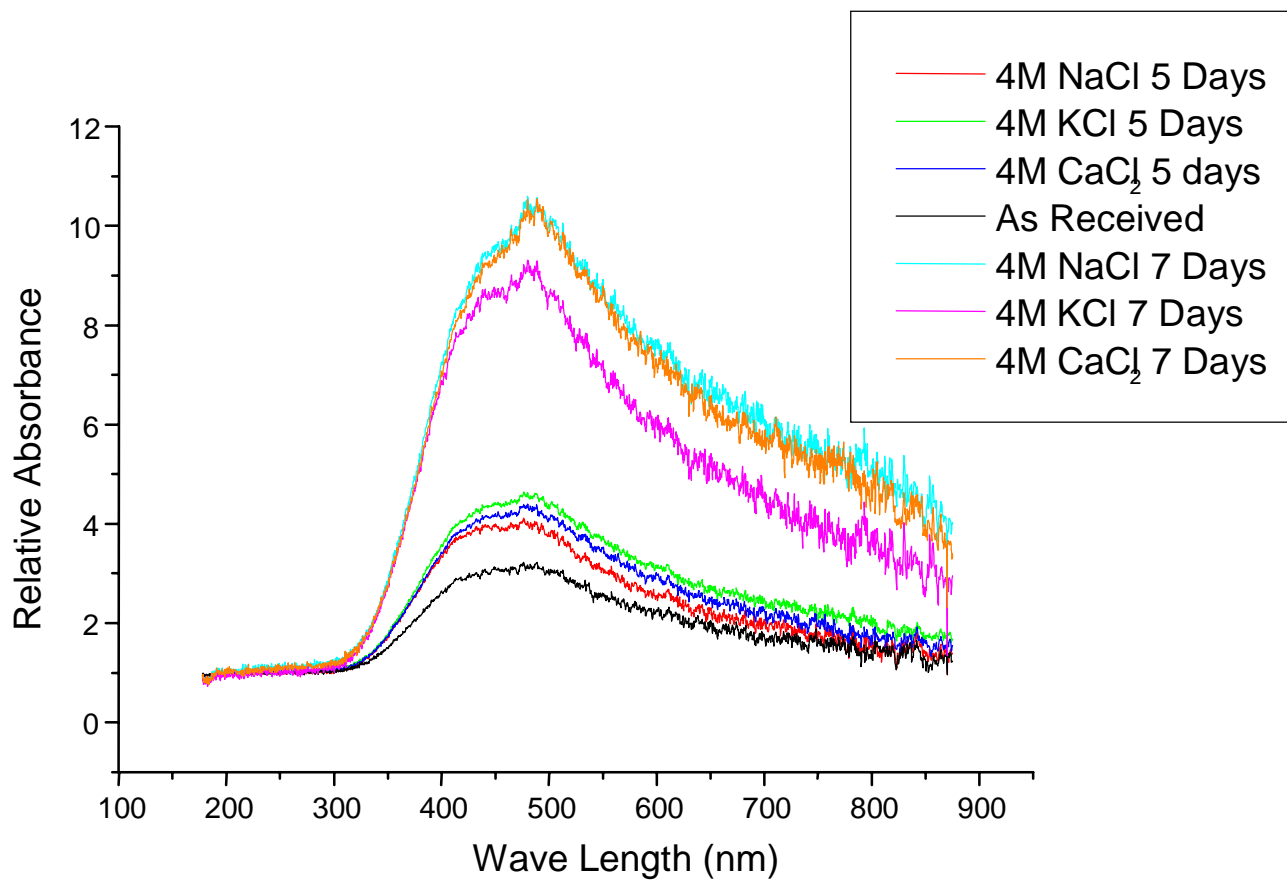


Figure 24 UV/Vis Absorption After Exposure to 4M Salts

3.7 Differential Scanning Calorimetry

The first DSC scans of samples that had been exposed to a salt solution, dried, and allowed to equilibrate to ambient conditions all showed a large endotherm at 100°C due to evaporation of water. The water evaporation endotherm was followed by another large endotherm centered at approximately 262°C with an average ΔH of 68 J/g (Figure 26). The only exception to this was for the films exposed to CaCl₂. They appeared to have a slightly smaller ΔH of approximately 65 J/g. The second DSC scans all showed a small endotherm at approximately 241°C with a ΔH of around 3 J/g. This endotherm was followed by an exotherm at approximately 243°C with a ΔH of about -2 J/g. After the exotherm there is a large melting peak at 262°C with a ΔH of about 59 J/g (Figure 27). As before the scans for the samples exposed to CaCl₂ had a slightly smaller ΔH of approximately 53 J/g.

The first DSC scans of samples that had been preheated in an oven at 300°C for 10 minutes and then quenched in liquid nitrogen all had an exotherm with a ΔH of between 4 and 5 J/g, but they all appeared to be in slightly different locations. The samples that had been exposed to either water, 4M CaCl₂, KCl or were untreated, had an exotherm on average at 238°C. The samples which had been exposed to either NaCl or 1M CaCl₂ had their exothermic peaks on average at 230°C. After the exothermic peak, each spectrum had an endothermic melting peak that is centered on average at 261°C, but with varying ΔH . The samples, which were exposed to either H₂O, 1M NaCl, CaCl₂, or were untreated had an average ΔH of 63.5 J/g. Nylon samples exposed to 4M NaCl or 1M KCl had an average ΔH of 55.3 J/g.

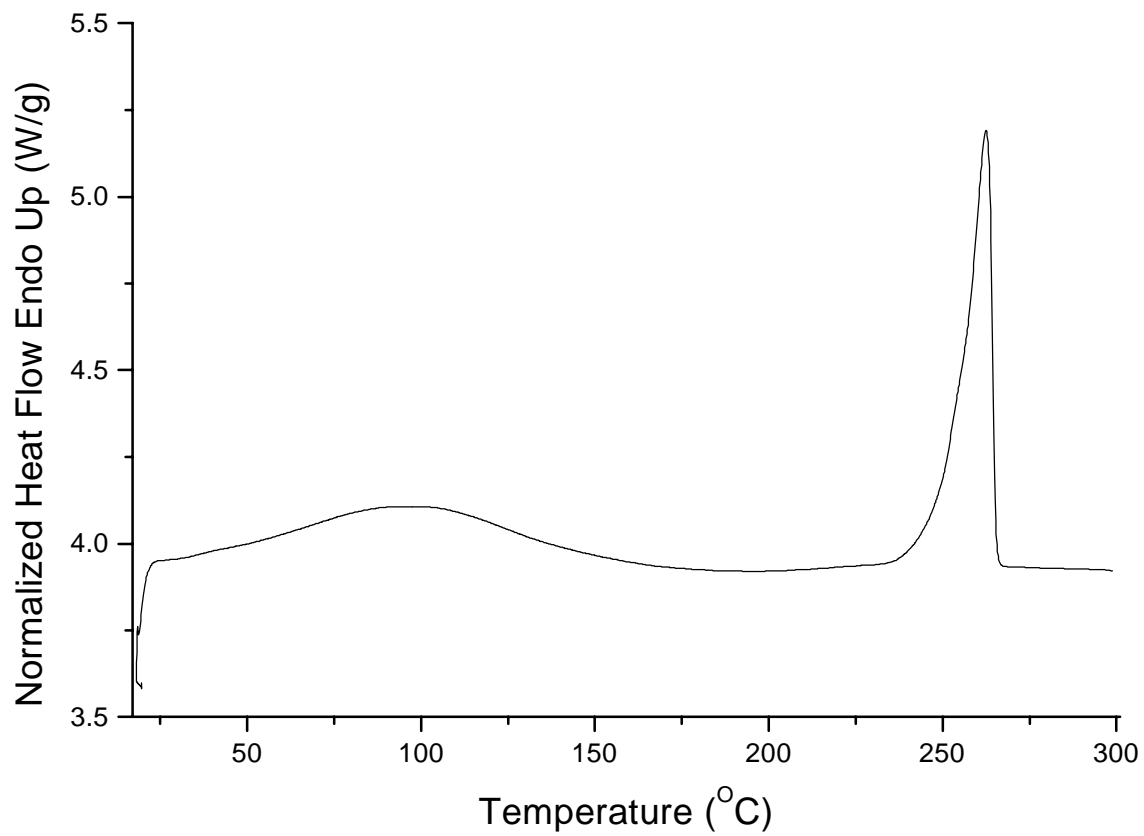


Figure 26 Typical First DSC Temperature Scan

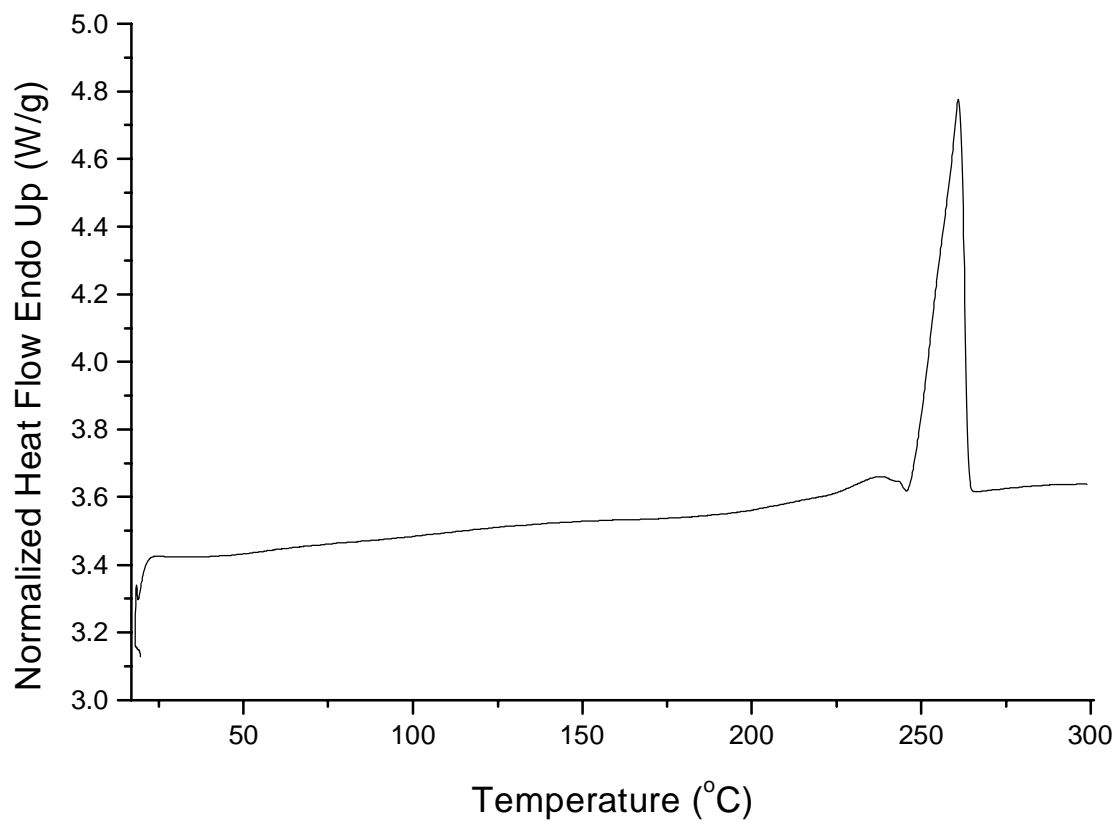


Figure 27 Typical Second DSC Temperature Scan

Finally, the sample which was exposed to 4M KCl had a ΔH of 44.8 J/g (Figure 28).

The second temperature scans of these samples resulted in spectra similar to the second temperature scans of the samples that had not been heated in the oven. All spectra had a small endothermic melting peak and a small exothermic crystallization peak similar in size and position as those occurring in the second heat scans of the samples not exposed to the oven conditions. After the endotherm and exotherm, a significant endothermic melting peak occurred on average at 261°C, but with varying ΔH . The samples that were exposed to 1M NaCl, H₂O, CaCl₂ or were untreated had a ΔH of 53.4 J/g, while those exposed to 4M NaCl or KCl had an average ΔH of 47.4 J/g.

The variation in the location of the crystallization exotherm in the first temperature scans of the pre-melted samples could be reflective of the degree of interference of the salt on the intermolecular hydrogen bonding of the samples. If the presence of the salt greatly interferes with the hydrogen bonding, then the chains should have greater mobility and thus crystallize at lower temperatures. The variation in the ΔH of melting for the endotherms in the first heat scan of the pre-melted samples could be reflective of two possible things. The first possibility is that some salts are retarding crystallization during the quench and thus decreasing the percent crystallinity in the sample, which would lower the ΔH of melting. The second possibility is that some salts induce defects in the crystalline structure, thereby lowering the amount of energy required to melt them. Finally, if we ignore the differences between the ΔH of melting for the various salts and just look at the average ΔH of melting on each run, we find that with each successive heating to 300°C, the ΔH decreases.

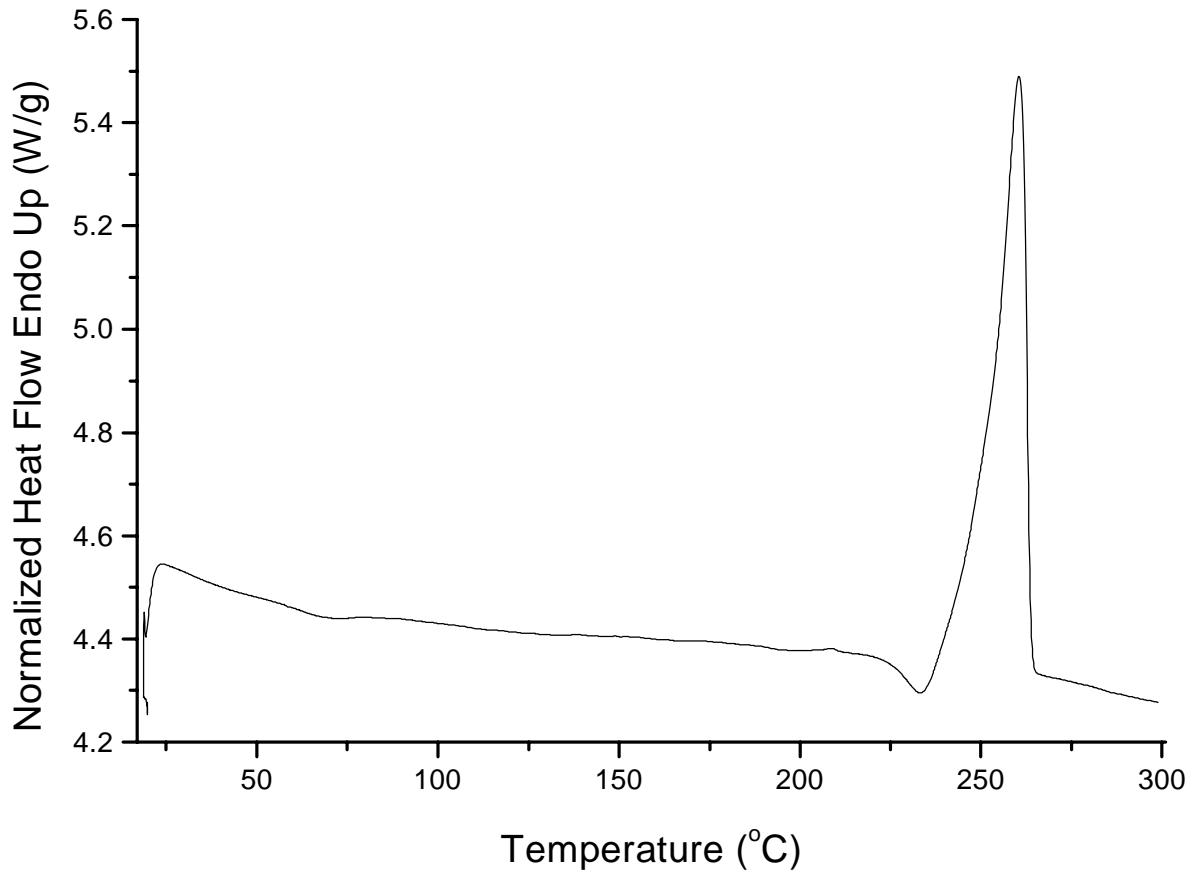


Figure 28 Typical First DSC Temperature Scan for a Quenched Sample

For example, samples that were not pre-melted and quenched had an average ΔH of 67.6 J/g during their first melt, but the second melt had an average ΔH of 58.5 J/g. The samples that were pre-melted and quenched had an average ΔH of melting of 58.8 J/g during their first temperature scan, which decreased to an average of 51.1 J/g for the melting during the second temperature scan. In looking at the results of the DSC data, it must be remembered that only the first heat scan of the samples that had not been previously melted are directly relevant to this project. After the initial melt, the salt can then become incorporated into the crystalline portion of the polymer, which is an unrealistic possibility when looking at the effect of salt splash.

3.8 Infrared Spectroscopy

The results of the reflectance IR spectra showed no significant change in the spectrum after exposure to any of the salts. In general, the peaks normally associated with nylon 6,6 could be discerned (Table 8) but they were often undetailed.

Table 8 Characteristic IR Absorptions for Nylon 6,6

| Location (cm⁻¹) | Origin |
|-----------------------------------|--------------------------|
| 1550 – 1541 | N-H Bending |
| 1650 – 1634 | C=O Stretching |
| 2900 – 3000 | C-H Stretching Aliphatic |
| 3100 – 3400 | N-H Stretching |

In addition to the peaks in Table 8, there were often other peaks at $2300 - 2400 \text{ cm}^{-1}$ and at $3500 - 3600 \text{ cm}^{-1}$ which were due to CO_2 in the atmosphere. The background subtraction feature was unable to completely subtract these peaks.

The attempts at using transmission IR spectroscopy were equally inconclusive. With these spectra, one could see the baseline and the bottom portion of the peak areas listed in Table 8. Unfortunately, the absorptions of the peaks were so large that all of the light in those frequency ranges was absorbed.

If we look at Beer's law (Equation 5), where A is absorbance, a is absorptivity, b is path length, and c is concentration, we see the origin of the problem.

$$A = abc \quad (5)$$

In order to decrease the absorbance of the sample it would be necessary to decrease either a , b , or c . However, the absorptivity and the concentration are fixed, leaving path length as the only quantity that can be varied. Unfortunately, since the experiments were being performed with a industry provided film, the thickness could not be altered without concerns about changing morphology.

Chapter IV

Conclusions

From this research we can draw several conclusions. First, from the moisture absorption curves found in Figures 9 and 10 we find that both the type of salt present and the concentration of the salt can have significant effects on the amount of moisture absorbed, which may be reflective of changes in the chemical potential of the salt solution. This absorption of moisture was found to be pseudo-Fickian in nature.

Secondly, it was found that the type and concentration of salt solution absorbed effected how the yield stress behaved with increasing exposure time. This reflected the amount of moisture absorbed by the samples, but not entirely, as shown in Figure 16. This fact suggests that there are other forces at work in addition to plasticization. Possibilities include a deterioration of the films with exposure time or perhaps an interaction between the nylon and the salt that acted to stiffen the chains, as was shown by Siegmann⁹ and by More¹⁰.

Attempts to determine the amount of residual salt present in the films after drying showed that the amount of salt picked up was significantly less than what was expected. This suggests that salt and water were not absorbed at the same rates. This conclusion is supported by the work of Wyzgoski and Novak¹³. In addition, little could be stated about the amount of residual salt that was retained due to the large experimental error in the mass measurement.

From the UV/Vis study of samples exposed to various salts, it was found that as they age the absorption increases. It appears that the presence of salt can accelerate aging and that the type of salt present has an effect on the degree of acceleration. However, it does not appear that the concentration of the original salt solution has a significant effect on the amount of deterioration. This, in part, could be reflective of the fact that the films pick up a relatively small amount of salt when exposed to either concentration, resulting in no discernable difference in aging. The varying effect of the different salts could be reflective of the degree of interaction between the salt and the nylon chains, but more work would be required to prove this. However, a mechanism of how the salt interacts the nylon to accelerate deterioration was proposed.

From the DSC studies we found that the presence of residual salt in the amorphous portion of the material had little effect on the melting behavior of the sample. However, after an initial melting, the salt appeared to have more of an effect on the melting behavior, lowering ΔH , reflecting its inclusion in the crystalline portion of the system. Once the salt was included in the crystalline phase, the type of salt present was found to determine the degree to which ΔH was effected. Also, the type of salt present in a rapidly quenched sample effects the location of the recrystallization peak. Finally, it was observed that with each successive heating, the ΔH of melting for the nylon samples decreased. These behaviors likely reflect the degree of interaction between the salts and the polymer, which again is a function of two forces, namely the interference of hydrogen bonding by the salts and the stiffening of the chains via complexation of salts with the chains. The interference with hydrogen bonding would tend to lower the crystallization

temperature, while also lowering the ΔH of melting. However, the stiffening of the chain through complexation with the salt would tend to increase the crystallization temperature and the ΔH of melting. Also, the lowering of the ΔH of melting with each successive run could be reflective of degradation of the material with heating.

Overall, from this research we can conclude that the effects we see at work are not so much the result of one thing but rather the combination of several forces. These forces are the plasticization of nylon by water, the complexation of salt with the polymer chain, and the degradation of the polymer with heating and aging.

Chapter V

Future Work

This research, while answering only a few questions, has pointed the way to several areas of potentially fertile research. One of the more promising areas would be to look at the effect of residual salt on the T_g of nylon 6,6. This could be done either through DMA or through dielectric studies. Preliminary dielectric studies of samples that had been saturated with either water or a 1M KCl solution and dried, suggested that residual salt greatly effects the conductance of nylon (Figure 29). However, not enough data was collected to allow any conclusions to be drawn about the effect of various salts on T_g or on conductance.

Another promising area of research would be to obtain thinner films, thus allowing successful IR studies of the interactions of the salts and polymer. Better data should be obtained for the amount of residual salt present in films. This could be accomplished by using either a more accurate balance or by using atomic absorption spectroscopy as was done by Wyzgoski and Novak¹³. Also, it would be useful to do mechanical tests on samples that had been dried after salt exposure, so as to determine how much complexation of the salt with the polymer chain stiffens the chain.

Finally, it would be useful to better understand the modes of deterioration of the film with salt exposure and heating. This might best be done by using either extraction techniques allowing removal of degradation products for further study or by looking at

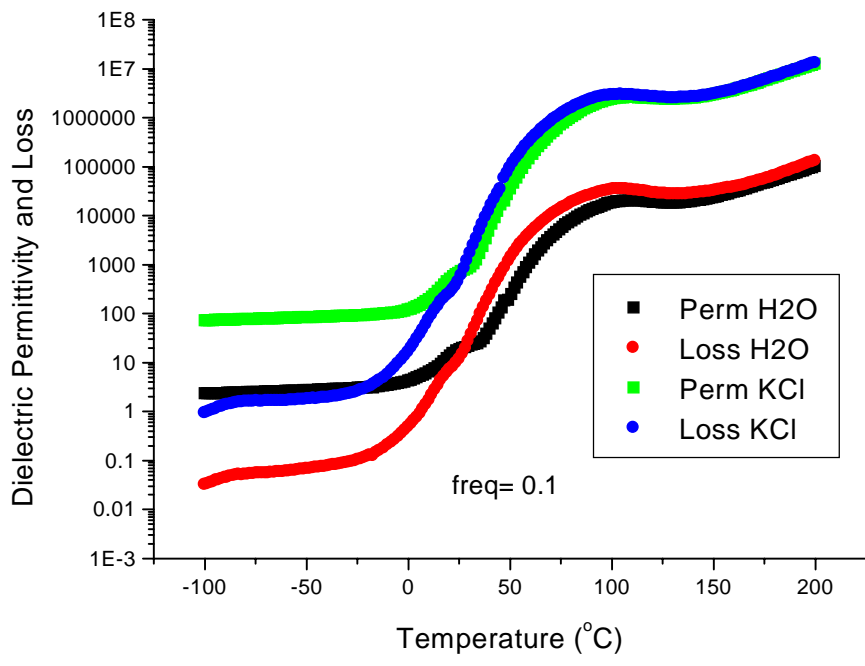


Figure 29 Preliminary Loss and Permittivity Curves

molecular weight distributions after exposures via GPC, as was done by Wyzgoski and Novak¹³.

Continuation of the DSC studies would, however, not be a good area in which to continue research. This study showed that residual salt had little to no effect on the melting behavior of nylon during the first melt. Any studies of melting after that are dealing with a system which may contain salt in the crystalline portion, and is thus unrelated to the initial heating scan and to the original goals of this study.

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