Chloramines: A Potential Pathway to Reusable Thermoset Elastomers

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Introduction

In today's world, the ideas of waste management and pollution are of large concern. One aspect of this is the large amount of waste going to landfills rather than being reused or recycled. The concern is the presence of plastics in landfills as plastic can take hundreds to thousands of years to break down. As a result, there is a focus on recycling plastics to reduce the amount of plastic waste being sent to landfills (Nkwachukwu et al., 2013).

The types of plastic that can be traditionally recycled are classified as thermoplastics. These plastics consist of long chains of molecules with no chemical bonding between the chains. This structure results in solid phase polymers that soften or melt when heated, allowing them to be reformed into other shapes or products with minimal reduction of structural properties.

Elastomers consist of chains like thermoplastics, but they have other covalent chemical bonds between the chains, locking their structure more strongly to the form of the reservoir they were contained in when they underwent chain linking or cross-linking. As such, when heated elastomers are considered permanent structures and do not melt or soften in a way that is useful for recycling or reforming, resulting in a much more complicated and expensive recycling process (Kroeger, 2013, p. 5). These recycling processes for elastomers are not economically viable so most elastomer waste either gets sent to landfills, buried on site for industrial equipment, submerged as starter reefs or burned for power. These alternatives might reduce volumes but are also harmful to the environment, and so it is important to find an alternative method of recycle elastomers that is economically viable.

Monochloramines have been explored as an alternative to chlorine as an industrial water disinfectant. It has been observed that the rubber seals and gaskets used in wastewater treatment plants that utilize monochloramines degrade at a higher rate than equivalent seals used in plants that use the more traditional chlorine disinfectants. This suggests that it may be possible to use monochloramines to accelerate the degradation of elastomers.

Several studies have noted the accelerated degradation of elastomers in a lab setting, giving more weight to the idea that monochloramines could be potentially used in an elastomer breakdown/recycling process. The initial studies used low concentrations of monochloramines in water, in the range of fifty to one hundred parts per million and were conducted to gauge the stability of the resins when exposed to the disinfectants. Though degradation occurred at these concentrations it was slow, requiring weeks of elastomer exposure to observe significant degradation (Reiber, 1993). These timeframes would not be viable in an industrial recycling process.

More recent research has used much higher concentrations of chloramine in water, about 1000-2000 ppm. This resulted in faster rates of degradation, allowing for significant portions of test samples to break down and dissolve into solution after a week of constant exposure to test solution (Kroeger, 2013, p. 77). This again gives more validity to the idea that monochloramine solutions may be able to be used in recycling elastomers.

These studies have shown that monochloramines can be effectively used to break down elastomers, however they lack a comprehensive look into what elastomer breakdown by-products are, whether the resulting particles can be reformed into a new product which addresses whether there is any residual unsaturation after breakdown, and whether any chloramine-based breakdown process is economically viable. In addition, there are still very few studies that look at this process, with only one study using more concentrated solutions.

The goal of this project was first to confirm the results found in the scientific literature, at both low and high concentrations, and second to analyze the products of the breakdown of the elastomer. This would give more credibility to this procedure, as well as provide more data to enable a feasibility assessment on chloramine-mediated breakdown of cross-linked elastomers.

Methods

The experimental process used consisted of three main experimental methods. The low concentration trials required a stock chloramine solution to be created, and an experimental plan to be run utilizing several different amounts of dilution of the stock solution. The high concentration trials utilized a modified method for creating a stock solution to create the much higher concentrations of monochloramines required. The high concentration trial did not make use of dilutions and had a different combination of samples than the low concentration trials. From these experiments, there is the potential to analyze the breakdown residues more comprehensively as well as to resolve gravimetrically what fractional breakdown existed. Finally, a swell testing method was used to track the bulk structure of the degraded elastomer samples. The expectation is that lower cross-link density after chloramine exposure would be manifested as a lower network crosslink density.

Low Concentration Trials

The low concentration trials used a stock solution of ~100ppm monochloramine in water. Three vials were run with full rubber bands submerged in the undiluted stock solution, three vials were run with full rubber bands submerged in a 3:1 dilution of stock solution to water, and three vials were run with full rubber bands submerged in a 1:1 dilution of stock solution in water.

Stock Solution. The stock solution for the low concentration trials was created using a modified version of the procedure listed in ASTM standard D6284-17. First, 990 mL of deionized water was added along with a stir bar to a one liter bottle. While stirring, 1.67 mL of 5.67-6% sodium hypochlorite solution and 2.09 mL 7 pH phosphate buffer solution were added to the water. After ten minutes of stirring, 1.41 mL 1N ammonium hydroxide solution was added along with an additional 4.18 mL 7 pH phosphate buffer solution. This stock solution was stored in a laboratory refrigerator to reduce the decomposition of the solution while in storage and was not kept beyond three weeks.

Test Samples. Each test sample consisted of a full rubber band, cut into linear sections 83 mm long, 1.5 mm wide, and 1.1 mm deep. Nine samples were grouped into sets of three, with the aim of making each triplicate as similar as possible. These samples were placed into 20 mL vials and labeled from one to nine. Samples one through three were added to the stock solution, samples four through six were dedicated to the 3:1 dilution outlined above, and samples seven through nine were dedicated to the 1:1 dilution outlined above.

Test Procedure. First, each vial was filled with 20 mL of test solution. The dilutions were prepared by adding deionized water to the stock solution in a 20 mL graduated cylinder, the resulting test solution was then added to the corresponding vial. 5 mL of deionized water was added to 15 mL of stock solution for the 3:1 dilution, and 10 mL of deionized water was added to 10 mL of stock solution for the 1:1 dilution. The vials were then placed into a laboratory oven that was set to 65 °C and left for 24 hours. After each 24 hour period the vials were removed from the oven, the spent solution within the vials was poured into a collection jar while the test sample was kept in the vial, fresh test solution was added to the vials, and the vials were placed back into the oven. The elastomer samples were exposed for a total of 144 hours, or six days. The trials were run for two days a time over the course of three weeks. A swell test was

performed on every test sample before the first exposure to the test solution, and after the last exposure to track the degradation of the test samples.

High Concentration Trials

The high concentration trials used a stock solution of 1000-2000ppm monochloramine in water. Three vials were run with full rubber bands, one vial was run with thirty-two rubber band, and a final vial was run with thirty-seven pieces of bicycle tire. All vials were run with undiluted stock solution, the two vials with cut elastomer utilized stir bars to keep the solution well mixed.

Stock Solution. The stock solution for the high concentration trials was created using a further modified version of the procedure outlined for the low concentration trials. First, 850 mL of deionized water was added along with a stir bar to a one liter bottle. While stirring, 32 mL of 5.67-6% sodium hypochlorite solution and 32 mL 7 pH phosphate buffer solution were added to the water. After ten minutes of stirring, 28 mL 1N ammonium hydroxide solution and an additional 50 mL 7 pH phosphate buffer solution were added to the solution. This stock solution was stored in a laboratory refrigerator to reduce the decomposition of the solution while in storage and was not kept for more than three weeks.

Test Samples. The three vials utilizing full rubber bands consisted of a full rubber band cut to be linear. The cut rubber band sample consisted of two rubber bands cut into 5-6 mm long sections, resulting in thirty-two pieces for testing. The cut bicycle tire sample consisted of a portion of a bicycle tire cut into thirty-seven pieces, each 8 mm by 6.5 mm by 2.5 mm which were rinsed before being used for testing. The three full rubber bands were placed into 20 mL vials while the cut rubber band and tire samples were placed into 50 mL vials.

Test Procedure. First, each vial was filled with the corresponding test solution. The 20 mL vials utilized 20 mL of undiluted stock solution as their test solution, and the 50 mL vials utilized 50

mL of undiluted stock solution as their test solution. The vials were then placed in an oil bath maintained between 65-70°C and left for 24 hours, keeping the 50mL vials under constant modest stirring. After every 24 hours, the vials were removed from the oil bath, the spent solution within the vials was poured into a collection jar while the test samples were kept in their vials, the vials were recharged with fresh chloramine solution, and the vials were placed back into the oil bath. Two separate collection jars were used, one for the rubber band samples and other for the tire sample. The vials were heated for a total of 98 hours, or four days. The trials were run for two days a time over the course of two weeks, as the oven used was only available for continuous twenty four hour periods over the weekends. A swell test was performed on the full rubber band test samples before the first exposure to the test solution, and after the last exposure to track the degradation of the test samples. The swell testing procedure is outlined below.

Swell Testing Procedure

First, the volume of the test sample is measured using calipers. Three measurements were taken in the smaller dimensions of the sample, one in the middle and one at each end. One measurement is taken along the length of the rubber band, which is defined as the longest dimension. The test sample is then submerged in tetrahydrofuran and is left for forty eight hours, making sure that the test sample stays submerged for the entire forty eight hours. Next, the volume of the test sample is once again measured in the same way as before the sample was submerged. Equation 1 was then used to determine the crosslink density ν of the sample. The Flory parameter χ was determined to be 0.44, the molar volume of the solvent V was determined to be 12.3, and the volume fraction of the swollen sample ϕ was determined by dividing the volume of the test sample after submersion by the volume of the test sample before submersion.

$$ln(1 - \phi) + \phi + \chi\phi^2 + \nu V(\phi^{1/3} - \phi^2) = 0 \qquad \text{(Equation 1)}$$

Results

The results for this experiment come in the form of the changes in crosslink density observed from the swell testing, and qualitative observations of the change in the color of the test solutions.

Swell Testing

In both the low and high concentration trials, the crosslink density was not observed to significantly decrease after being exposed to the monochloramine solutions, as seen in Figure 1. The significance of this observation, and potential causes of this will be discussed below.
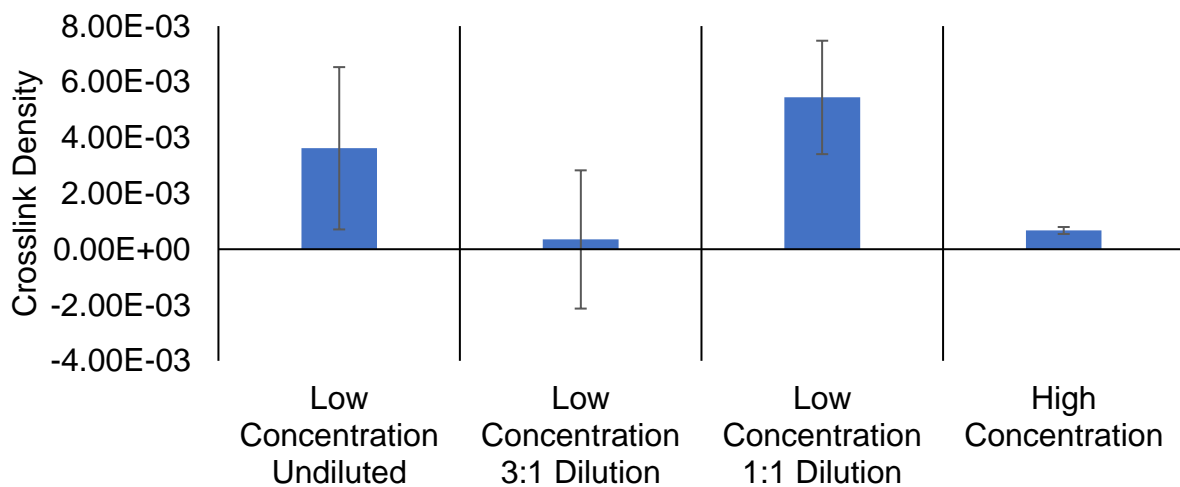

Figure 1: The average change in crosslink density for each test solution with error bars

resembling standard deviation.

Color Change

The two vials of cut elastomer samples in the high concentration trial changed color during each twenty four hour period. The significance of this will be discussed below, and one example of the color difference can be seen in Figure 2.

Figure 2: Vials with fresh solution (left) and after twenty four hours (right)

Discussion

The results of the swell testing suggested that no significant degradation of the elastomers occurred, which is not what was expected based on previous studies. However, the color change observed suggests that there is some reaction occurring in the cut elastomer samples.

Swell testing

As mentioned, the results of the swell testing suggested that no significant degradation occurred. The expected behavior based on previous studies would be that the crosslink density would decrease with exposure to monochloramine solutions. Instead, the trials resulted in either an increase in crosslink density or no significant decrease in crosslink density. This would suggest that monochloramine solutions are not effective in breaking down elastomers. However,

there are a few potential explanations for why this has occurred, either due with issues in performing the swell testing, or with performing the degradation experiments.

Swell Testing. The main issue with the performed swell testing is that it relies on the test samples being dry, as the volume change occurring is assumed to be due to the sample absorbing the tetrahydrofuran. As the test solution was comprised of water, any residual water remaining in the structure of the sample could reduce the reliability of the swell testing.

Experimental Method. There are two potential issues with the performed experimental method, the lack of stirring during testing and an unknown true concentration of the stock solutions. The lack of stirring during the testing of the full rubber bands was intentional. As successful swell testing relies on the accurate measurement of the test samples, damage sustained to the samples due to a stir bar would hinder the effectiveness of the swell testing. As the test samples became more brittle when saturated, this was a justified concern that led to stir bars not being used with the samples that swell testing was performed upon. Though this may have contributed to the observed results, it is unlikely that this would have had such a large effect as it would have only slowed the reaction which does not explain why the crosslink density was observed to increase in several cases. It is also possible that the stock solutions used were not of the concentration expected through stoichiometry and scaling known procedures. This is a result of monochloramines being inherently unstable, as is the sodium hypochlorite that is used to make the monochloramine solutions. At the time the experiments were initially run, I did not have access to the required equipment to measure the strength of the stock solutions. As such, it is possible that the stock solutions were at a lower concentration than expected throughout the testing. As with omitting stir bars, this would reduce the rate of reaction through the trials and would not account for any increases in the crosslink density but could reduce the total amount of degradation that occurs.

Color Change

Though the swell testing did not suggest that degradation was occurring, the color change that occurred in the solutions exposed to the cut pieces provided more optimistic results. The fact that the color change occurred means that the monochloramine solution is having some effect on the test samples. It is possible that this effect is limited to leaching additives such as carbon black, zinc, or silica out of the test samples. However, many of the particles that settled to the bottom of the collection jar resemble small fibers, suggesting that either the test solutions are successfully degrading the samples or that there are other forms of reinforcements included in these commodity elastomers. However, the extent of degradation and the makeup of the recovered particles are currently unknown and will be the focus of further research.

Future Research

Due to the time limitations present in this project, the extraction and characterization of particulate out of the spent monochloramine solutions is incomplete. However, these next steps are planned to be performed in the fall term 2022. First, liquid-liquid extraction will be performed using hexanes. This would both purify the extract, separating potential resin from the chemicals used to form the monochloramine solutions, and move the potential resin into an easily vaporized solvent. Next, the hexanes would be removed through vaporization techniques to acquire a dry sample. The resulting residue will be characterized by IR spectroscopy and other techniques to analyze its composition and dilute solution viscometry to find the average molecular weight of the recovered resin. Finally, an attempt would be made to crosslink the resin to confirm that it is possible to do so. Once these further experiments are complete, it would be possible to perform a feasibility study on the process, which is one of the main goals of the project.

Conclusion

The quantitative evidence observed so far seems to suggest that no significant degradation is occurring in the test samples from the low concentration chloramine solutions. However, the color change and observations of particles found and recovered from the high concentration trials suggest that some form of degradation can be achieved. I am at a natural stopping point given the end of the term and an upcoming internship, but I intend to return and address the characterization of the degradation by-products next term. This can also include the characterization of recovered resin.

References

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