

Biomass-Based Sustainable Polymers to Reduce Plastic Waste

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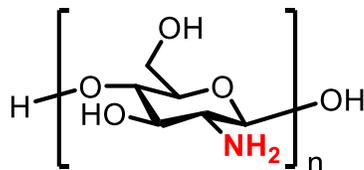
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Abstract

The amount of plastic waste consumed annually is astronomical, in fact, the “seventh continent” refers to the large piling of plastic waste in the Pacific Ocean. This project aims to synthesize more sustainable and resourceful polymers, and so chitosan-based polymers are analyzed. Chitin can be extracted from shrimp or crab shells and chitosan can be prepared from chitin with an alkali treatment. Chitosan is a renewable resource and since it is biocompatible it will not cause future problems like traditional plastics. Populating the literature are chitosan hydrogels used in applications ranging from environmental to biomedical. Examples of biomedical applications include tissue engineering, drug delivery methods, and 3D printing; while, environmental applications include pollutant absorption and enriched soil for plants. Chitosan has been documented in the literature to couple with aldehydes and epoxides. These crosslinkers are ideal for a green solution because they are miscible in water too. This is important because the desired polymer will, therefore, be biodegradable and reduce overall waste. The molar ratio of chitosan (amide) to crosslinker is very important for the structure of the polymer because the structure of the film is dependent on the amount of coupling between the two reactants. For example, an aldehyde crosslinker has been the most efficient reaction, immediately reacting with the chitosan solution; however, based on the amide- aldehyde molar ratio, this did not always prove to be a sturdy material. The molar ratios between amide to crosslinker are still being analyzed, however, multiple films have been successfully produced with relative flexibility and strength. The amide to crosslinker molar ratio will be further examined and manipulated to produce a desired sturdy and flexible polymer to help reduce plastic waste.

Keywords: Biodegradable, Polymerization, Cross-linking

1. Introduction

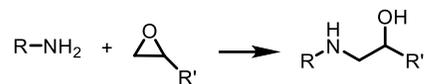


Scheme 1: The schema for the structure of chitosan.

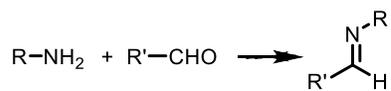
Chitosan is the second most abundant mineral⁶ on the Earth; and the known applications are increasing linearly. One of the most common sources of chitin is in the shells of crustaceans. This makes for a great polymer base because of its abundance and accessibility. Most notably, chitosan has been cited for having applications in the biomedical field and novel plastics¹⁻⁶. For example, chitosan-based links are referenced in three-dimensional printing (3D) for hydrogel microstructures^{7, 8}, and 3D applications alone range from novel 3D printing material to guided cell growth^{7,8}. Other highly studied areas within the biomedical field include tissue engineering and drug delivery^{9,10}. Since chitosan is

biocompatible it can be used in the environment freely without releasing harmful toxins. Research has been conducted to take advantage of the naturally adsorbent hydrogel for environmental purposes. In some cases the hydrogel can absorb up to six-times its own weight in water and can also aid in plant growth^{11,13}. It is proposed, most commonly, that chitosan-based hydrogels could be used to clean toxins out of bodies of water by absorbing toxins^{12,13}. Once the toxins are removed from the water via the hydrogel, the gel could be washed, reused, and the toxins could be disposed accordingly. Applications of the absorbency can range from the pharmaceutical industry with encapsulation of a targeted molecule to the environmental field to remove pollutants¹³. As noted already in the literature, chitosan has many desirable characteristics which is what prompted the interest in this project.

Moreover, chitosan from shrimp shells is about \$10-15/ kg which is about 3-4 times the cost of other synthetic polymers⁵. However, unlike nylon 6, LDPE, or PE, chitosan is a fully compostable material and could even be sold as plant fertilizer to enhance plant growth because of its high nitrogen composition⁵. Although it is expected that the price of biopolymers, including chitosan, will decrease over time due to the current push for more resourceful materials⁵. Also, in favor of biopolymers, the price of synthetic polymers is expected to increase over time because of their oil derivative nature. Furthermore, this means that the possibility of chitosan as a future biopolymer is not unreasonable. The research we have been completing has coupled numerous crosslinkers with chitosan at varying ratios to determine the ideal combination for practical applications. Below is an outline of the procedure followed.



Scheme 2: The proposed reaction between an amine (found in chitosan) and an epoxide.



Scheme 3: The proposed interaction between an amine (found in chitosan) and an aldehyde.

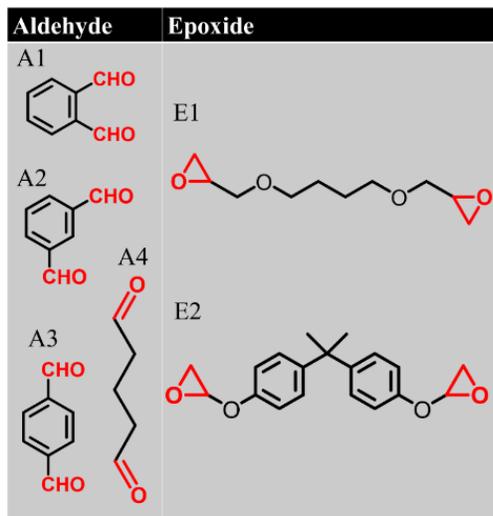
2. Methods

2.1 Preparation Of The Chitosan Solution

Three different chitosan solutions were prepped: one, two, and three weight percent. Each had 100.0 mL of deionized water and 1.00 mL of acetic acid. The weight percent of chitosan was determined by the amount of chitosan and 1.00g, 2.00 g, and 3.00g were added respectively. Multiple batches of each solution were prepped over time however this should not be a significant source of error between different experiments.

2.2 Pairing The Chitosan Solution With Numerous Crosslinkers

The chitosan solution was paired with many different crosslinkers, but mainly dialdehydes. See Scheme 4 for most notable crosslinkers used. The applicability of each crosslinker was analyzed using a gradient ratio. For example, if a new crosslinker was being tested then some weight percent would be increased on a steady gradient while the chitosan weight percent was held constant. Moreover, the weight percent of the crosslinker would stay constant while the weight percent of chitosan in solution would vary. Once this data was found, the best ratio could be determined and analyzed further with greater precision. The procedure used to dry the chitosan-crosslinker solution varied between a glass petri dish and a silicon coated paper box.



Scheme 4: The most notable crosslinkers paired with chitosan.

2.3 Analyzing The Resulting Films

The films were analyzed using infrared spectroscopy (IR), tested for their mechanical properties, and viewed using scanning electron microscopic images (SEM). The outcomes of these tests are detailed in the results section.

3. Results

In general, it was found that *o*-phthalaldehyde (A1) crosslinked with chitosan had the most desired results, (Figure 1) in comparison to the other dialdehydes that were experimented with. The films formed had little to no air bubbles. Figure 1b had air bubbles that lined the outer edge but was relatively sturdy compared to other films with similar compositions. Figure 1a had a very little amount of air bubbles but was more fragile in comparison. Figure 1a also was also dried using a glass Petri dish, while Figure 1b was dried in a handmade paper box. The box was harder to regulate because it had to be newly made each time and because of this the exact dimensions and flatness of each box could be slightly different. The glass Petri dish also proved to be less reliable than originally thought because films would continue to be thicker around the edges than in the middle. It is possible that a modified procedure could be a solution, and this can be explored in further research.

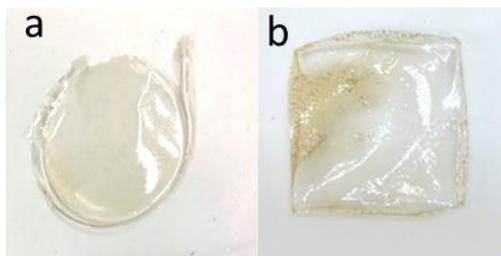


Figure 1: The morphology of the resulting chitosan-based films containing a) 2.4 mmol of chitosan and 0.012 mmol of *o*-phthalaldehyde and b) 0.8 mmol of chitosan and 0.05 mmol of *o*-phthalaldehyde.

Figure 2 validates the physical results reported. The most important functional group in chitosan in this reaction is the amine group. The IR spectrum (Figure 2c) of chitosan shows the N-H peak in the starting material. Similarly, the *o*-phthalaldehyde IR spectrum was taken to show the carbonyl peak in the starting material. The product's IR spectrum shows a C=N peak which means that there is a new bond that was not present in the starting materials; and according

to Scheme 3 this C=N bond was expected. Additionally, the N-H and C=O peaks found in the starting material are not in the IR of the product and that validates that the reaction had proceeded to completion. SEM images were taken of a film with chitosan and o-phthalaldehyde (Figure 2a). The image shows the microscopic features within a few hundreds of micrometers which showcases the uniformity of the film, which is the ideal outcome. This is important because the more homogeneous the film, the more wholistic analysis can be completed. Additionally, the mechanical properties for the film shown in Figure 1a can be seen in Figure 2b. These results are not ideal because each trial should be identical since they are prepared from the same sample. The tensile strain for the sample ranges from about 6-10 mm/mm and the tensile stress ranges from about 30-90 MPa. The film itself could have possibly had different properties on different sections of the sample. For example, when the films were prepared in the round, glass Petri dishes it was observed that the outer edges of the film had a greater thickness than the inner portion. If the film is thicker in one trial than another than that could result in uneven data as presented in Figure 2b. Future research will need to avoid this consequence.

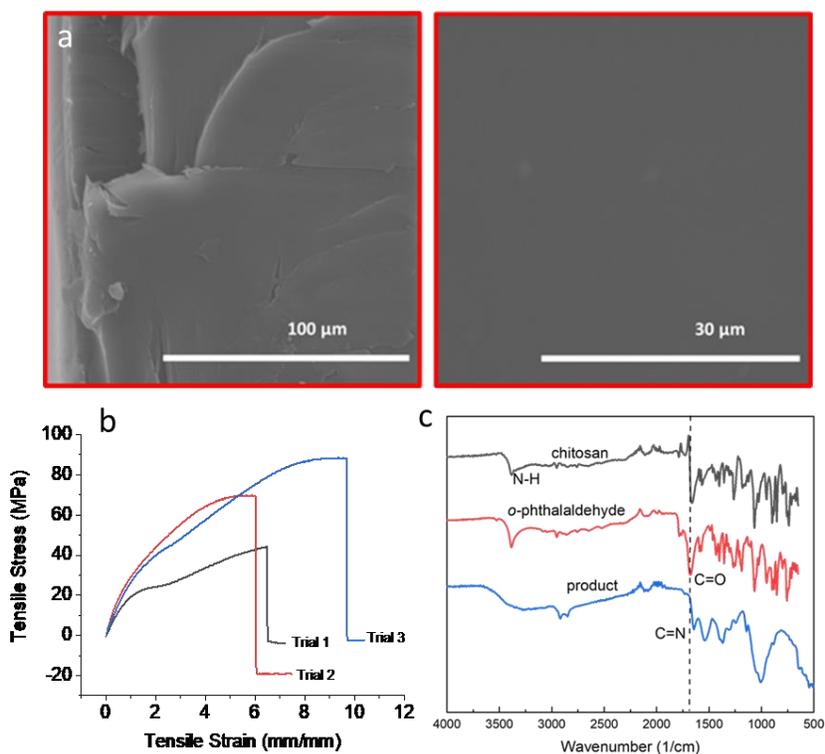


Figure 2: The data recorded for films crosslinked with o-phthalaldehyde: a) SEM images: left is a cross-sectional image and on the right is a plainer view, b) the mechanical properties of Figure 1b, and c) IR of the reagents and product.

When isophthalaldehyde (A2) and terephthalaldehyde (A3) was cross-linked with chitosan the resulting gel did not dry into a smooth, homogenous film, but instead a hard, curled material (Figure 3). The mechanical properties of the film could not be tested as a result of the inconsistency in thickness and shape.

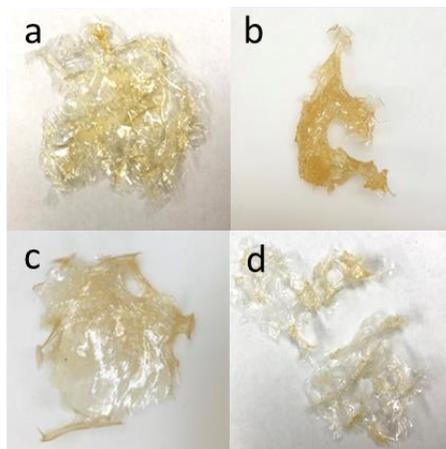


Figure 3: The morphology of the chitosan-based film with isophthalaldehyde and terephthalaldehyde: a) 2.4 mmol of chitosan and 0.15 mmol of terephthalaldehyde, b) 2.4 mmol of chitosan and 0.12 mmol of terephthalaldehyde, c) 2.4 mmol of chitosan and 0.12 mmol of isophthalaldehyde, and d) 1.2 mmol of chitosan and 0.075 mmol of isophthalaldehyde.

After these results were observed, PEO and wood composite were physically mixed into the solutions in order to compare the possible changes that would result in their respective films. PEO was mixed with dialdehydes 1-3 listed in Scheme 4. This was completed at numerous molar ratios, but the most notable and morphology of the various experiments are below in Figure 4a-c.

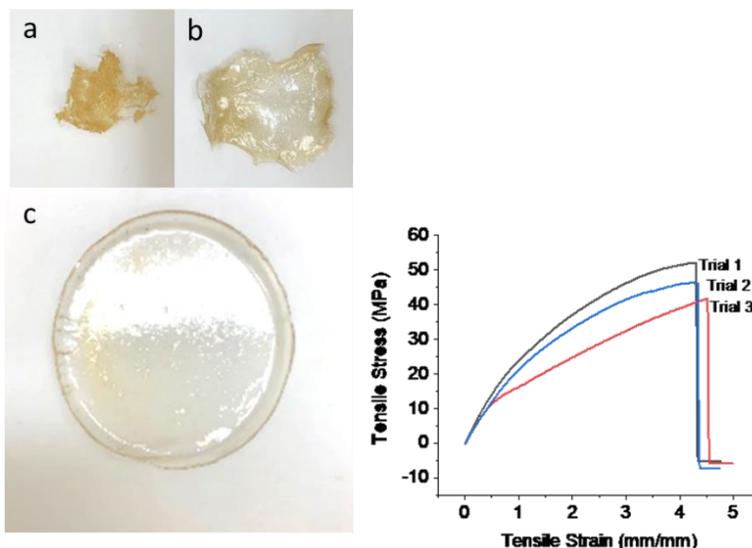


Figure 4: The resulting morphology of the chitosan-based films (2.4 mmol) and 0.0015 mmol of PEO with various crosslinkers including 0.012 mmol of terephthalaldehyde (a), isophthalaldehyde (b), and o-phthalaldehyde (c) (left); and the mechanical properties of film c (right).

It may be tempting to conclude that the film shown in Figure 4c the most effective because it had limited air bubbles, while the films without the PEO (Figure 1) had air bubbles lining the outer rim of the film. However, this is a difficult comparison to make because the molar ratio between the two reagents are different and therefore cannot be accurately compared directly because there could be other reasons for the phenomena. However, the films shown in Figure 4 can be directly compared because the only difference between the three were the dialdehyde used. Therefore, the previous conclusion that terephthalaldehyde and isophthalaldehyde were not ideal crosslinkers with chitosan was applicable

and apparent even when PEO was added in addition. The mechanical properties were taken for the film shown in Figure 4c and can be seen to the right.

Although not perfect, the mechanical properties shown in Figure 4 are relatively similar, in comparison to other tests. Each trial dropped off around 4.5 mm/mm but varied between a tensile stress of 40-55 MPa. Ideally these values should be the same in each trial since it is from the same sample. However, this is progress from Figure 2. As noted, wood composite was also added to the dialdehyde mixture in hopes to increase mechanical properties. Although the gel formed was visibly smooth and seemed well mixed, the film did not demonstrate these properties. The resulting film had air bubbles, wood particles on the surface, and was not flexible (Figure 5).

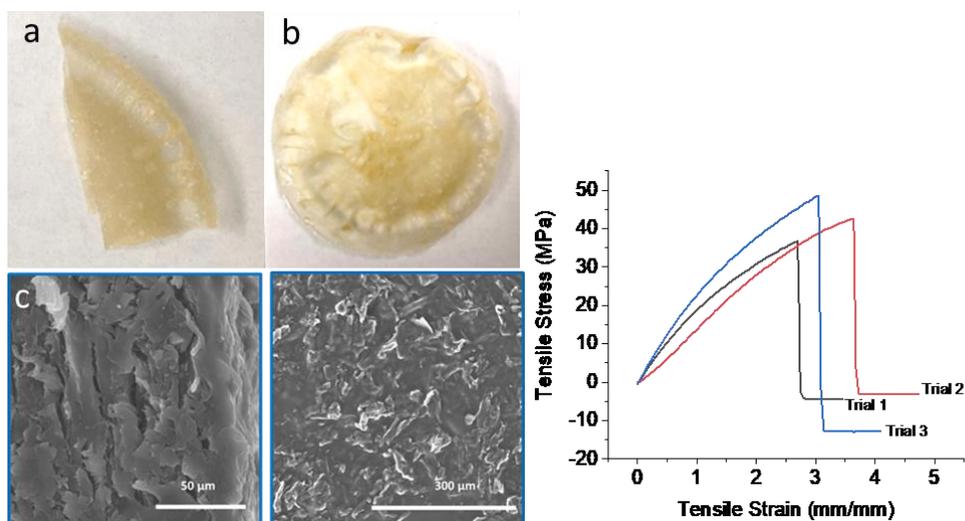


Figure 5: The resulting morphology of the chitosan-based film with 2.4 mmol of chitosan with various o-phthalaldehyde and wood composite amounts: a) 0.48 dialdehyde and 180 mg of wood composite and b) 0.24 mmol dialdehyde and 150 mg of wood composite (top left). The SEM images (bottom left) and mechanical properties (right) are shown for film a. The left SEM image is a cross-section and the right image is a plainer view.

As seen in Figure 5a and 5b, the films limited the accuracy of further testing. The film from Figure 5a was tested for its mechanical properties and can be seen in on the right. The tensile strain ranged from about 2.5-3.5 mm/mm and the tensile stress ranged from about 20-50 MPa; and as noted earlier the trials should be closer together because they are prepared from the same film. SEM images were taken of film with chitosan, o-phthalaldehyde, and wood composite and showed the wood particles suspended throughout the film (Figure 5c). Further research will be needed to provide more accurate data.

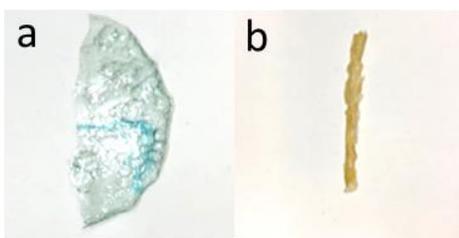


Figure 6: The resulting morphology of the chitosan-based films crosslinked with epoxides: a) 1.6 mmol of chitosan, 1.2 mmol 1,4-Butanediol diglycidyl ether (E1), and 0.06 mmol of copper (II); b) 0.8 mmol chitosan, 0.1 mmol bisphenol A diglycidyl ether (E2), and 0.3 mmol of o-phthalaldehyde.

As mentioned before, epoxides were also paired with chitosan, however these results were not as successful and resulted in undesirable results. Figure 6a was too fragile with numerous air bubbles, and Figure 6b was too curled and hard to test or manipulate further.

4. Future Work

Future research will explore the chitosan-dialdehyde interaction through more experimentations with o-phthalaldehyde specifically. However, these experiments will be using different as well as repeated molar ratios to construct more accurate and reliable data. Molar ratios and procedures will be repeated to collect more data to support or reject data previously collected. Additionally, the molar ratios may remain the same while the procedure does not. This method would allow for an improved procedure to ensure the films are strong, flexible, and homogeneous throughout. Inevitably new molar ratios will be tested, first with known procedures and then with modifications. The known procedures will keep the dependent variable as the new crosslinker and once that is known then the dependent variable can be changed to the procedure itself.

Ideally, the film would be homogenous, like mentioned above, which means that the air bubbles currently in multiple of the films would need to be removed. This would improve the accuracy of the mechanical properties testing, scanning electron microscopic images, and infrared spectroscopy data; and with improved accuracy the methods can be better conformed to fit the future existing problems until the films are applicable.

5. Conclusion

Overall, according to the data, the dialdehydes were a more effective crosslinker than the epoxides for this application. It was found that the crosslinking molar ratios were crucial and could be used to predict the outcome of the film. The most effective crosslinker was o-phthalaldehyde, which highlights the importance of stereochemistry. For example, isophthalaldehyde and terephthalaldehyde were also used under the same conditions and did not produce as desirable results even though both dialdehydes were on a benzene ring. Furthermore, it was found that 2.4 mmol of chitosan paired with 0.012 mmol of o-phthalaldehyde was not as desirable as 0.08 mmol of chitosan paired with 0.05 mmol of o-phthalaldehyde. In this case, it was better to have similar molar amounts of each reagent rather than much more chitosan. More experiments and replications will need to be completed for more accurate and conclusive results.

The data collected showed uneven mechanical properties throughout a single sample. This is problematic because the mechanical properties should be uniform across a sample, especially for industrial use. More experiments need to be run in order to find a general trend and to also dismiss this issue. Strong conclusions cannot be drawn from the mechanical properties data alone, except that further research is necessary. The SEM images also have a similar issue, where these images can only determine the relative porosity of the surface. This is hard to analyze objectively since the film samples themselves are not homogenous so one section of the same film sample may look different than another. However, the IR spectrum of the reagents and product does confirm that the reaction occurred completely. This is encouraging because this means that the reagents acted as predicted and that unknown side reactions are unlikely to occur.

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7. References

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