



Degradation of Plastic Polymers Using Green Heterogeneous Catalysts

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Introduction

The plastic waste problem has become an urgent environmental issue in the United States and around the world. According to Lytle¹, in the world, roughly 300 million tons of plastic are consumed and approximately 8 million metric tons of plastic end up in the ocean yearly; this number is expected to be 20 times greater by 2025. These plastic polymers take 500-1000 years to degrade naturally¹. Direct disposal of plastic polymers in landfills and oceans has led to pollutants like plastic aggregates, polymer microparticles (e.g., in micrometer sizes), and plastic chemicals, which could be dangerous to living beings. Plastic polymer waste in the ocean kills millions of ocean creatures (sea birds and marine mammals) yearly and 93% of Americans age 6 or older have tested positive with bisphenol A, a plastic chemical, in their body². Currently, synthetic polymer wastes are being degraded into small molecules (e.g., liquid fuel) primarily through pyrolysis. However, this process needs the consumption of high energy and could be hazardous in operation. Hydrogenolysis reaction (i.e., using H₂ reduction to break down polymers) has been proven effective for the degradation of biomass polymers, but has not been extensively used for the degradation of plastic polymers. For example, Dr. Dequan Xiao's group designed a new green catalyst (e.g., Cu-Fe-Zn alloy) that can break down lignin polymers under relatively mild conditions (200 °C) along with hydrogen³. This green catalyst was used along with hydrogen to test for the effectiveness of the degradation of plastic polymers in polymers like Polypropylene (PP), Polyurethane (PU), and Polyethylene Terephthalate (PET). This method can provide a new waste processing technology with mild working conditions.

Experimental Design

The experimental setup for the reaction can be seen in Figure 1. The setup contains a 300 mL (-1/+100 bar; -10/+300C) metal reactor, heating tape, hotplate, temperature control system, and an Omega® thermometer. Placed inside of the reactor were a stir bar, methanol, 3% Cu/Fe/Zn catalyst, and a polymer (PU, PET, or PP). The reactor was then flushed with argon and then filled with 20 bar H₂. The reactor was heated to a specified temperature (150°C, 175°C, 200°C, 240°C) for 4 hours to degrade the polymers. After allowing the reactor to cool overnight, the products were isolated and purified via vacuum filtration and rotary evaporator. They were then analyzed with FTIR and ¹H-NMR, which can be seen in Figures 6, 7, 12, and 13.

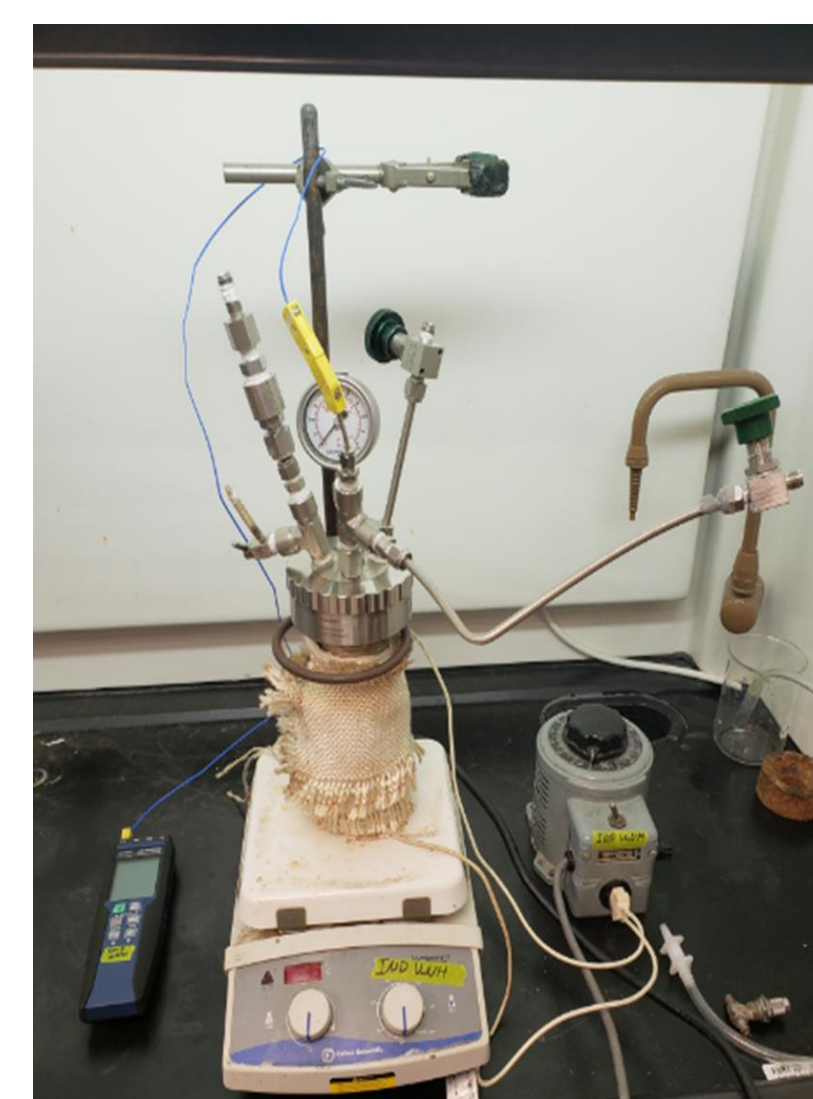


Figure 1: Experimental Setup

Results

Poly(ethylene terephthalate) - PET

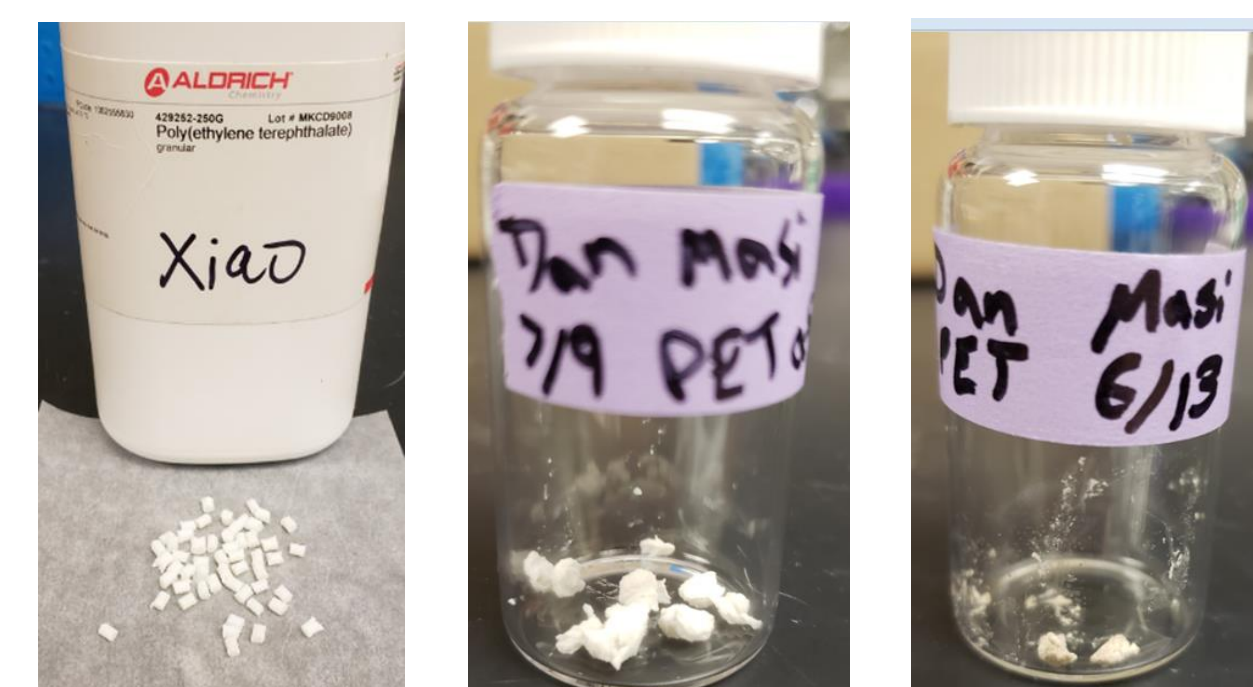


Figure 2: PET before reaction

Figure 3: Products from reaction at 175°C

Figure 4: Products from reaction at 200°C

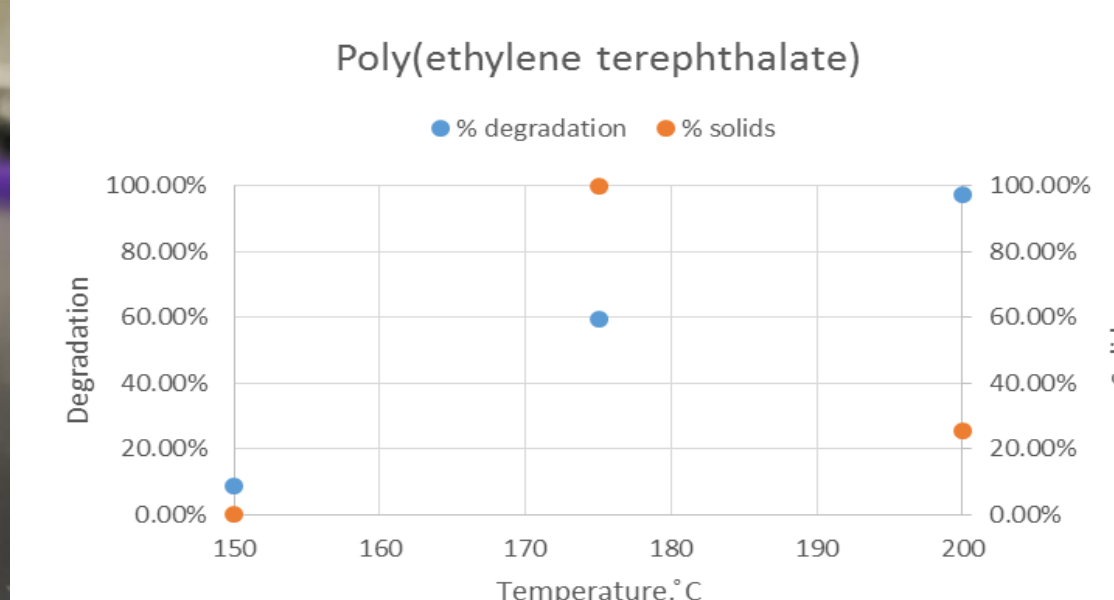


Figure 5: Percent Degradation & amount of products for PET at various temperatures

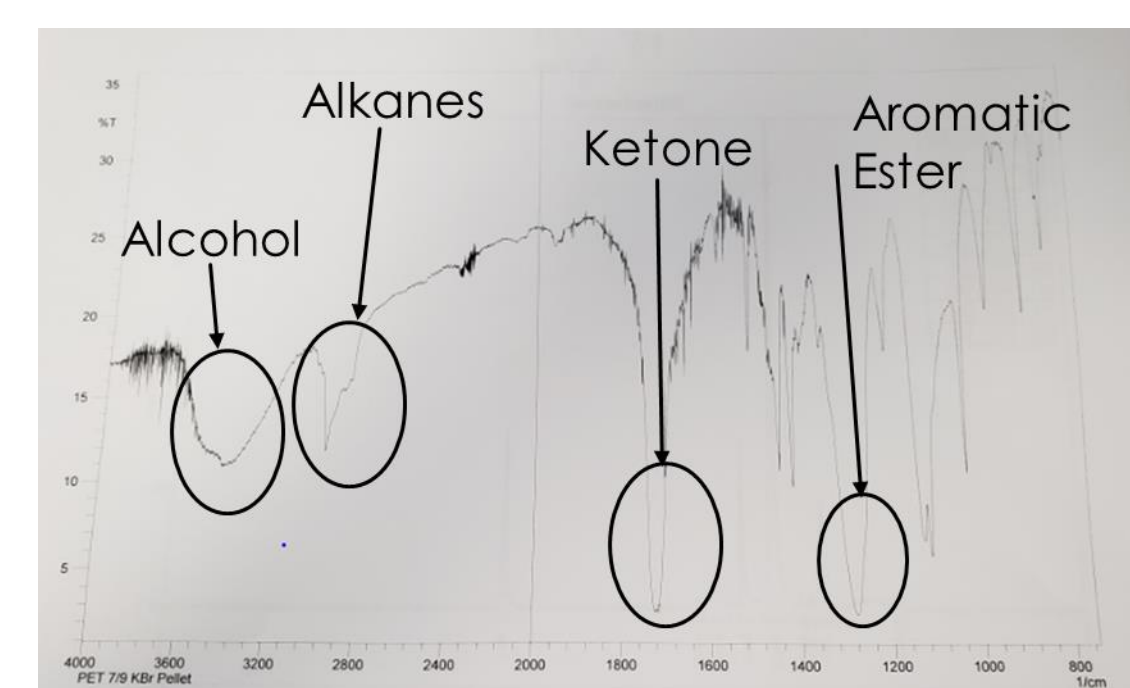


Figure 6: FTIR Spectrum for PET when the reaction was done at 175°C

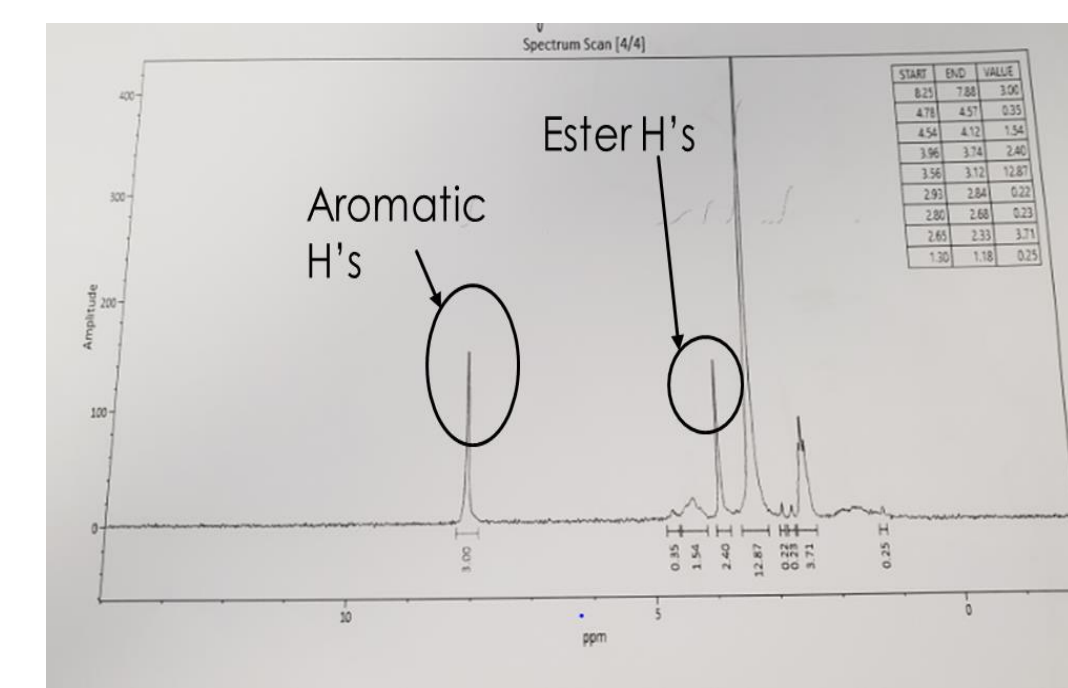


Figure 7: ¹H-NMR Spectrum for PET when the reaction was done at 175°C

Polyurethane - PU

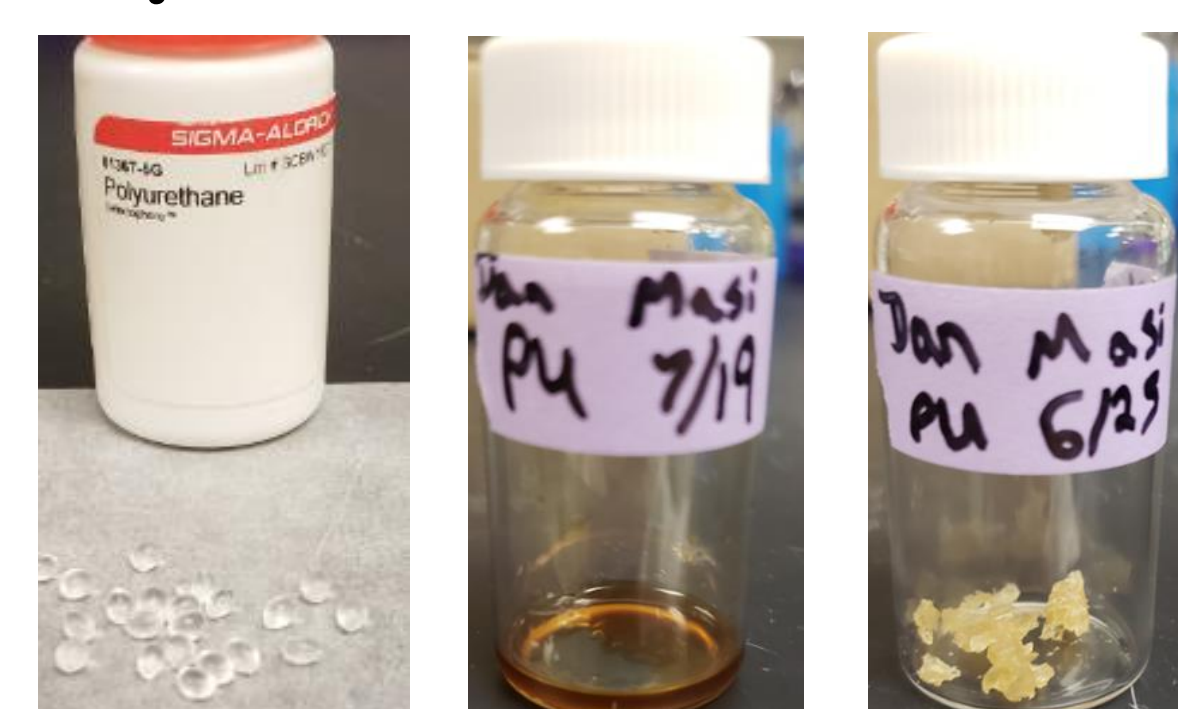


Figure 8: Polyurethane before reaction

Figure 9: Products from reaction at 175°C

Figure 10: Products from reaction at 200°C

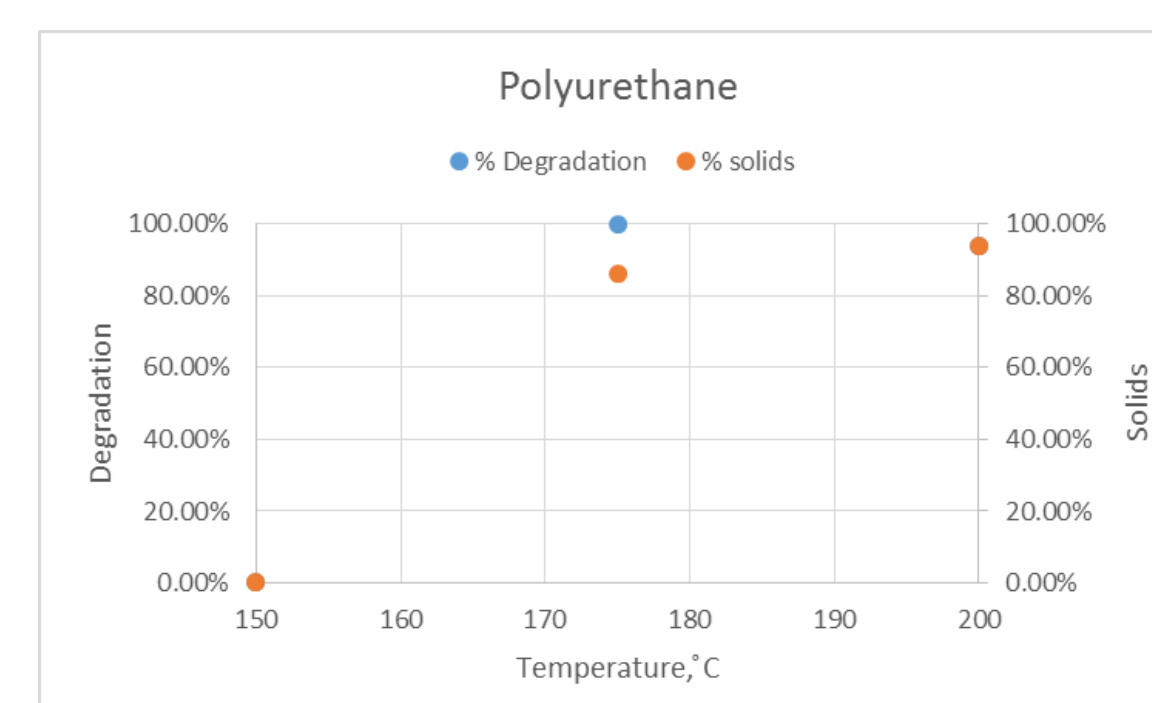


Figure 11: Percent Degradation & amount of products for Polyurethane at various temperatures

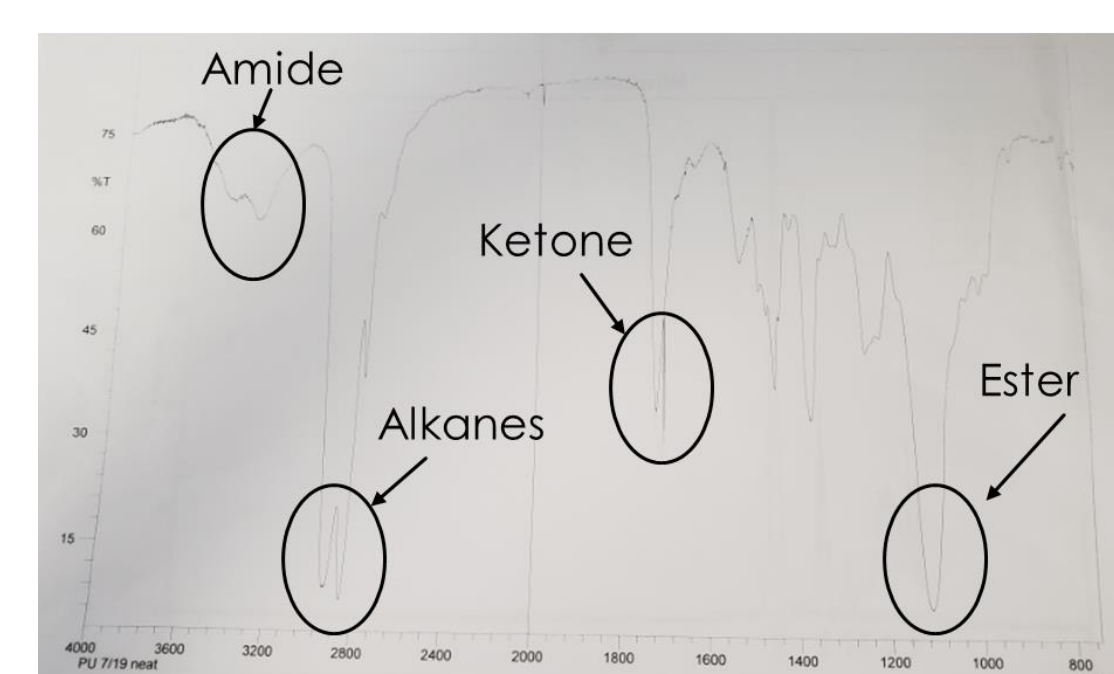


Figure 12: FTIR Spectrum for Polyurethane when the reaction was done at 175°C

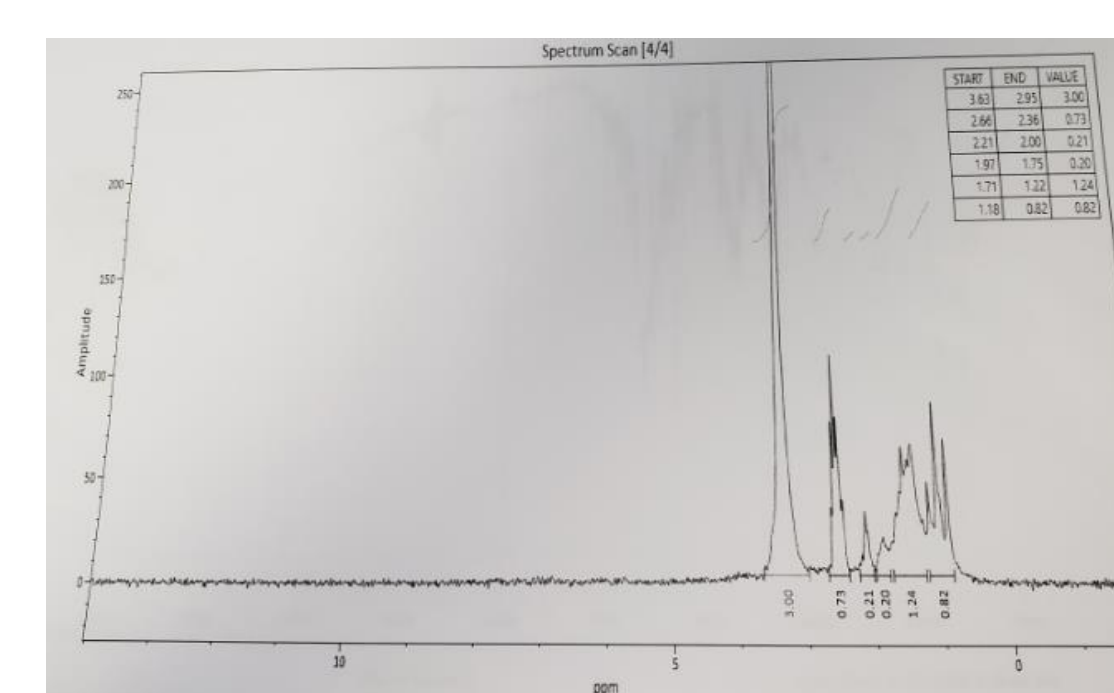


Figure 13: ¹H-NMR Spectrum for Polyurethane when the reaction was done at 175°C

Polypropylene - PP



Figure 14: Polypropylene before reaction

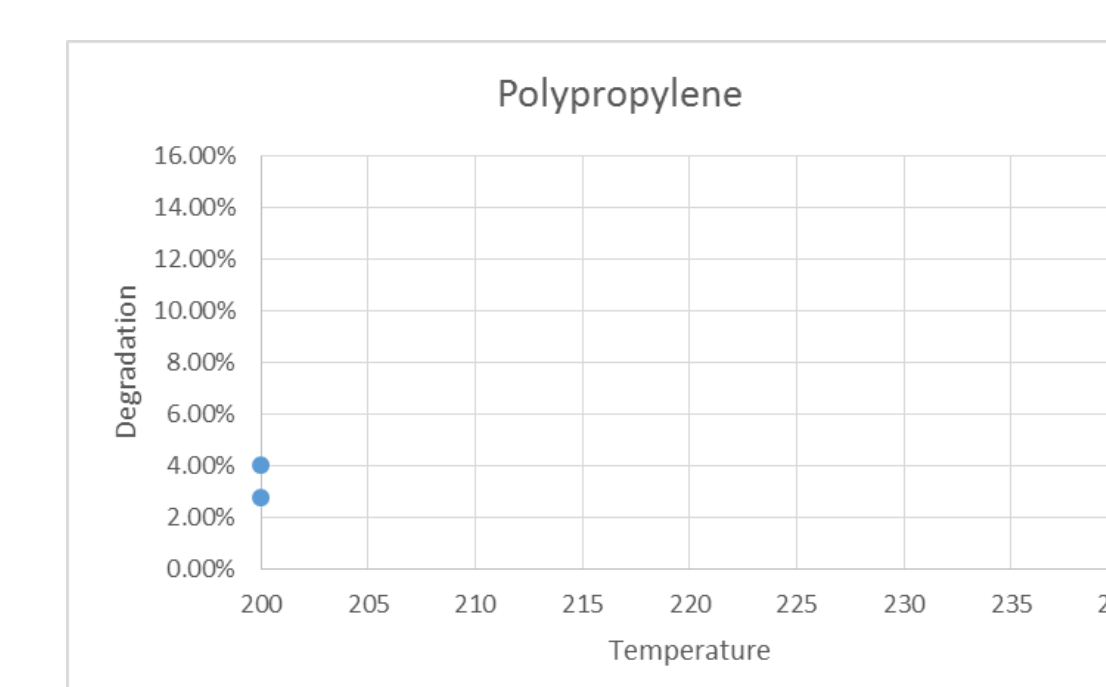


Figure 15: Percent Degradation of Polypropylene at various temperatures

Discussion & Conclusion

Throughout the research, it was discovered that hydrogenolysis can effectively break down ester or amide linkages in polymers, leading to the degradation of polymer esters or polyurethanes. However hydrogenolysis was not effective against C-C bonds in polypropylene. For PET and PU, respectively, high conversion yields > 90% were obtained at relatively mild reaction conditions (e.g., 200°C and 20 bar H₂). Urethanes showed to have a greater degradation rate than esters, which had a much greater degradation rate than C-C bonds. From FTIR and NMR analysis of PET, it can be seen that the degraded products contain aromatic esters, ketones, and alcohol functional groups. From the FTIR and NMR spectra of PU, it can be seen that the degraded products contain amides, ketones, and ester functional groups, but there appears to be no aromatics. This research provides a promising new solution to convert waste polymers found in packaging materials of peanut butter, soda, and insulation products into value-added chemicals in mild conditions.

References

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- [2] D'Alessandro, N. (2014, April 07). 22 Facts About Plastic Pollution (And 10 Things We Can Do About It). Retrieved February 13, 2018, from <https://www.ecowatch.com/22-facts-about-plastic-pollution-and-10-things-we-can-do-about-it-1881885971.html>
- [3] Petitjean, L., Gagne, R., Beach, E. S., An, J., Anastas, P. T., & Xiao, D. (2017). Quantum Chemistry Analysis of Reaction Thermodynamics for Hydrogenation and Hydrogenolysis of Aromatic Biomass Model Compounds. ACS Sustainable Chemistry & Engineering. doi:10.1021/acssuschemeng.7b02384

Acknowledgements

I would like to thank the University of New Haven and SURF for the opportunity they gave me. I would also like to thank Dr. Xiao for being an exceptional mentor, helping me through the duration of this project and for providing me lab space at the Integrative Materials Discovery Center. Lastly, I would like to thank Dr. Cirillo, Johnny Chang, and Michele Berman for the help they provided me.