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Analytical Techniques to Observe the Chemical Biodegradation of Thermoplastic Polyurethane Resins: FTIR, NMR, and SEM

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Analytical Techniques to Observe the Chemical Biodegradation of Thermoplastic Polyurethane Resins:  
FTIR, NMR, and SEM

A thesis submitted in partial satisfaction of the requirements for the degree Master of Science

in

Chemistry

by

Jenna J. Shepherd

Committee in charge:

Professor Robert S. Pomeroy, Chair

Professor Jerry Yang

Professor Kimberly Schurmeier

2022

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Thesis Approval Page

The thesis of Jenna J. Shepherd is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

University of California San Diego

2022

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## List of Abbreviations

PET: Polyethylene Terephthalate

TPU: Thermoplastic Polyurethane

FTIR: Fourier-Transform Infrared Radiation

SEM: Scanning Electron Microscope

NMR: Nuclear Magnetic Resonance

PVC: Polyvinyl Chloride

TAG: Triglycerides

CR: *Candida rugosa*

PU: Polyurethane

THF: Tetrahydrofuran

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## Preface

This work was done alongside Algenesis Materials, a company that has developed renewable and biodegradable polyurethane plastics in footwear. This research was only possible with the contribution of many UCSD faculty in the Department of Chemistry & Biochemistry and employees of Algenesis Materials.

## Acknowledgments

I would like to acknowledge Professor Skip Pomeroy for his guidance throughout my undergrad and graduate school experience. Thank you for giving me the opportunity to research in your lab during a global pandemic, and thank you for your continued support. I would also like to thank Professor Schurmeier and Professor Yang for being a part of my committee.

I would also like to express gratitude to the members of Skip's lab for the continued motivation and friendship we have acquired over the past two years. I would also like to thank Marissa Tessman for her mentorship, support, and constant reminders to upload my work to the drive. Thank you to Payton Evans, as I could not have asked for a better undergraduate assistant.

Thank you to Food and Fuel for the 21<sup>st</sup> century for financial support of this project.

Abstract of the Thesis

Analytical Techniques to Observe the Chemical Biodegradation of Thermoplastic Polyurethane Resins:

FTIR, NMR, and SEM

by

Jenna J. Shepherd

Master of Science in Chemistry

University of California San Diego, 2022

Professor Robert S. Pomeroy, Chair

The market for sustainable, biodegradable materials is steadily increasing as the world brings attention to the accumulation of plastic waste. Synthetic, polymeric materials that can be molded and shaped define plastic; it is estimated that 11 million metric tons of plastic are thrown into the ocean yearly.<sup>1,2</sup> Certain plastics, such as PET or Styrofoam, are not biodegradable, as their chemical structure can resist attack from microorganisms and the natural environment.<sup>3,4</sup> Although non-biodegradable, these plastics can be synthesized using recycled or bio-based materials, categorizing them as sustainable. Other plastics, such as polyurethanes and polycaprolactones, have a chemical structure that can be subject to

attack by microorganisms and break down naturally. Biodegradable plastics can also be synthesized from recycled or bio-based materials, classifying them as sustainable, biodegradable plastics.

This thesis demonstrates analytical techniques to observe the chemical biodegradation of sustainably synthesized thermoplastic polyester polyurethane resins (TPU) by FTIR, SEM, and NMR. FTIR was an instrument used to observe the urethane functional group coming apart into their respective biodegradation products. NMR was used to identify biodegradation products and observe changes to the remaining polyurethane skeleton due to degradation. SEM was used to monitor physical changes to the TPU, including cracks, crumbles, and microorganism growth.

## Chapter 1: Introduction

### 1.1 Background

Nylon, PVC (polyvinyl chloride), and plastics are all examples of synthetic polymers whose advancements have revolutionized the consumer goods industry. Since its invention in 1907, plastic has been known to be a cheap alternative to natural materials. It has allowed the working class to afford goods like jewelry, furniture, and board games.<sup>5,6</sup> Plastic has dominated as material produced globally; 400 metric tons are produced annually. Unfortunately, about 90% of plastic is not recycled, and more than 11 metric tons are thrown into the ocean yearly.<sup>7-9</sup> The impact of coastal and oceanic plastic waste heavily affects the marine ecosystem, as plastic litter can directly and indirectly harm marine wildlife through entanglement, ingestion, and general interaction.<sup>10</sup> The applications of bio-based, biodegradable plastics are becoming common as a way to mitigate the damage done to the environment from plastic waste generation.

### 1.2 Polyurethanes

Polyester-based thermoplastic polyurethanes (TPU) are a subset of incredibly versatile plastics. Their properties can act as a “bridge between rubber and plastic.”<sup>11</sup> TPUs are commonly used for insulation as rigid foams but can also be the primary polymer for shoes and mattresses; in Europe, polyurethanes are equivalent to polyethylene terephthalate (PET found in food containers) in terms of plastic consumption.<sup>12</sup> TPUs are thermoplastics, a subset of plastics that become pliable at hot temperatures and harden upon cooling, allowing them to be molded into any shape. TPUs are synthesized from a polyol, diisocyanate, and chain extender shown in Figure 1.

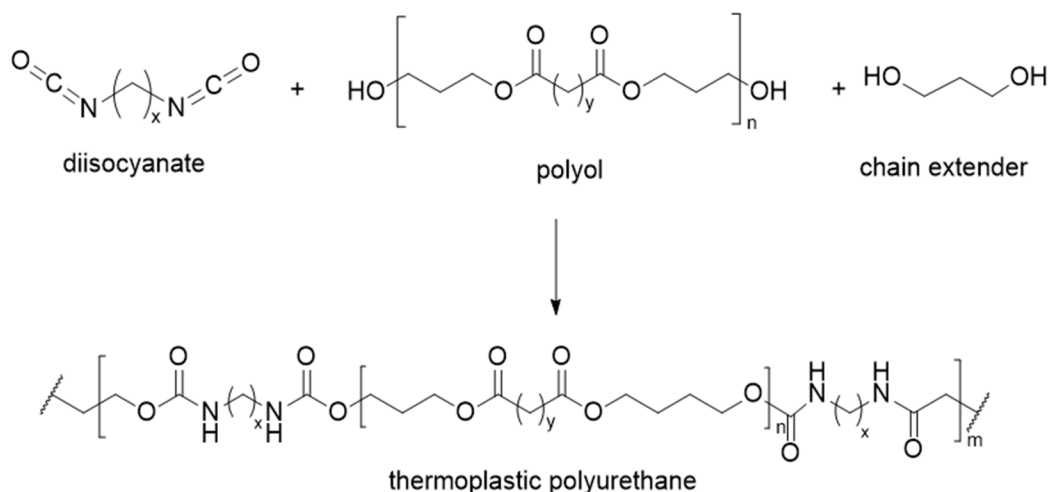


Figure 1: Synthesis of a general TPU<sup>13-15</sup>

TPU material is a two-phase microstructure caused by the formation of a soft segment and a hard segment within the polymer structure. The phase separation occurs due to the strength of the urethane moieties' hydrogen bond network, resulting in a crystalline structure (hard segment). In contrast, the flexible soft segment provides an amorphous domain (soft segment).<sup>16-19</sup> Changing the concentration of the reagents can control the physical properties such as tensile strength and elasticity of the final TPU.

The hard segment amide-ester urethane (carbamate) moiety is responsible for the strength and hardness of the TPU, while the soft segment polyol provides elasticity and tensile strength. The functional groups in the TPU presented in this thesis are shown in Figure 2.

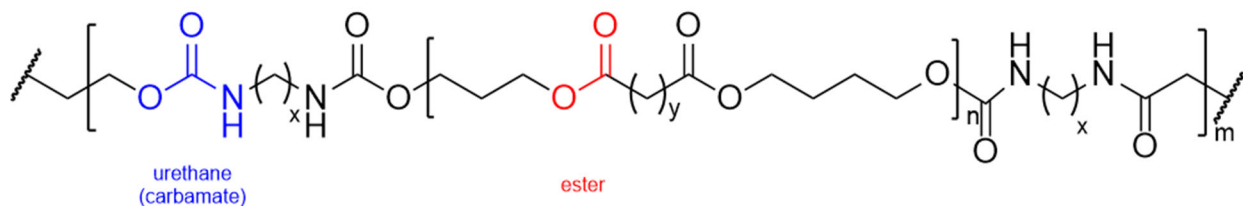


Figure 2: Urethane moiety (blue) and ester moiety (red) shown within a general TPU resin

### 1.3 Bio-based TPUs

TPUs can be synthesized from various materials, but using renewable sources is becoming of interest to TPU manufacturers for sustainability. Algae is one possible bio-based source for starting materials, as it can grow very fast in non-potable water, only requires sunlight and CO<sub>2</sub> to flourish, and can grow on non-arable land. Algal biomass waste can be converted into TPU raw materials, flavorings, and fuel.<sup>20</sup> From the algae waste stream, Triglycerides (TAGs) can be hydrolyzed into saturated and unsaturated fatty acids, which can then be oxidized into carboxyl to hydroxyl functional groups, resulting in a wide variety of applications. In the case of this TPU synthesis, TAGs were hydrolyzed into palmitoleic acid, which was then subject to ozonolysis to synthesize azelaic acid, which can then undergo acid-catalyzed polycondensation with a short-chain diol to create the polyol as a plastic precursor.<sup>20,21</sup>

### 1.4 Biodegradation of Polyurethanes and the Chemistry of Amides

Biodegradation is commonly quantified using a respirometer; a tool used to measure carbon dioxide exchange. Respirometers cannot be used to understand the chemical mechanism of biodegradation, and it cannot detect bonds being broken and/or formed. This thesis describes two analytical instruments to detect changes in functional groups and hydrogen atom locations (FTIR, NMR) and one analytical instrument to magnify the macromolecule enough to clearly see the breakdown of the TPU by nature.

The chemical structure of TPUs contains many hydrolyzable bonds at the carbonyl group of both the carbamate and the ester bonds, allowing for microorganism degradation. Analyzing biodegraded polyurethanes is possible because the amide that forms from the hydrolysis of the urethane bond is chemically unique, and its signals are easily recognizable by FTIR and NMR spectroscopy.<sup>22-24</sup> The carbon-nitrogen bond in amides is very different from amines because of the resonance stability of the carbonyl. The C-N bond distance within a urethane is 1.34 Å, which is right between the distance of a typical C-N single bond and a C=N double bond. This slightly shorter single bond length is due to the resonance stability of the neighboring carbonyl group, which also inhibits free rotation around the nitrogen by over 10 kcal/mol, resulting in a lower signal in FTIR at room temperature.<sup>22</sup> It can sometimes

correlate to two signals in an NMR spectrum (Fig. 3). Amides also show three distinct peaks in FTIR spectra, making the two analytical techniques an excellent way to observe the biodegradation of TPUs. It is also possible to observe the physical degradation of TPUs using scanning electron microscopy (SEM).

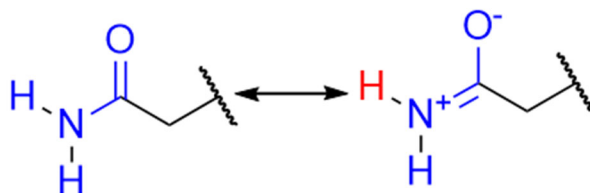


Figure 3: The resonance structure of amide bonds prevents free rotation around the N. This phenomenon causes two distinct peaks in NMR and a lower carbonyl signal in FTIR.

### 1.5 Conclusion

The accumulation of plastic waste is disrupting the marine environment and ecosystems as 11 million metric tons enter the ocean every year. Plastic manufacturers are looking for new ways to create sustainable, biodegradable plastics in all material applications.

This thesis aims to explain the analytical techniques used to evaluate the chemical biodegradation of renewable polyester-based thermoplastic polyurethane resins. SEM and FTIR are used to analyze two TPUs that have been composted for three weeks. 1D and 2D  $^1\text{H}$  NMR are used to analyze enzymatically degraded TPUs from *Candida rugosa* lipase enzyme.



## Chapter 2: Analysis of compost degraded TPUs by FTIR and SEM

### 2.1 Introduction to FTIR and SEM

Functional groups are unique groups of atoms on a molecule responsible for chemical reactions and physical properties. Characterizing an unknown compound from its functional groups can tell a general amount of information about the compound, such as its reactivity and stability. Ketones, esters, carboxylic acids, amines, and alcohols are common organic functional groups.

Analytical instruments utilize a stimulus on a molecule to produce a signal, which can then be interpreted to analyze its chemical properties. A common physical stimulus to excite organic molecules is electromagnetic energy; it does not contain mass, so the only detectable response on the instrument is from the molecule – the stimuli are ignored.<sup>25</sup> Shining an infrared light onto a molecule will cause covalent bonds to absorb specific frequencies of IR light and cause stronger molecular vibrations, producing a signal and outputting a graph or spectra. Fourier Transform Infrared Spectroscopy (FTIR) is an instrument that detects the covalent bond response of IR stimuli and uses a mathematical process to produce a spectrum from raw data. Covalent bonds can vibrate radially, longitudinally, and latitudinally, all detectable by FTIR.<sup>26</sup> FTIR is a fantastic analytical tool that can measure the progress of reactions by seeing a change in functional groups. Running a sample on FTIR only takes about 3 minutes and is relatively inexpensive compared to other analytical tools. Each molecule presents a molecular fingerprint in FTIR spectra, and two pure compounds can be determined to be the same compound if all FTIR peaks are the same.

While FTIR is a great tool to analyze functional groups, its use is limited to only IR active functional groups. Only polar bonds are detectable by FTIR because producing a signal requires a change in dipole moment. FTIR cannot give details about the compound, such as its molecular mass or structure, so it must be used with other spectroscopy techniques to characterize the entire molecule.

The biodegradation of polyurethanes can quickly be analyzed by FTIR spectroscopy, as the breakdown of the polymer produces changes to the molecular structure. Depending on the monomers

used to synthesize the PU, functional groups on polyurethanes can vary. Still, all PU have ester and amide functional groups, no matter the monomers used, due to the nucleophilic substitution reaction of the isocyanate and the polyol to form the PU.<sup>14</sup>

It is known that PU degradation happens through urethane ester bond cleavage to form an amide, which is then broken down into the parent amine (See Figure 3). This change in functional groups can be seen in FTIR spectra, utilizing the three distinct peaks that amides produce. The presence of the C-O bond in urethanes affects the polarity of the C=O bond and the C-N bond because of oxygen electron characteristics. The removal of the C-O bond is visible in FTIR spectra.

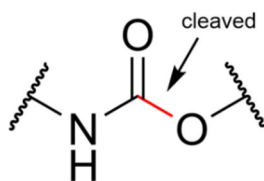


Figure 4: Urethane ester bond cleavage in the degradation of TPUs.

A scanning electron microscope (SEM) is used to look at samples at very high magnification. Unlike traditional microscopes that use light to form an image, an SEM produces a focused beam of electrons under a high vacuum sent towards a sample producing X-rays. The X-rays and scattered electrons can be detected, creating a high-quality image. SEM requires the sample to be conductive, so it is necessary to prep the TPU sample before imaging by coating it in a thin metal layer using a sputter coater.<sup>27</sup>

Two TPUs, TPU 14 and 32, were degraded in compost and analyzed via FTIR and SEM to show evidence of biodegradation. Structures of TPU 14 and 32 are shown in Figure 4.

## 2.3 Experimental

### 2.3.1 Polymer Synthesis

TPU 14 and 32 were synthesized similarly; there is a difference of one carbon in the polyol precursor. The synthesis was performed without a catalyst to slow down the curing time and control the final shape of the TPU. The previously synthesized polyol (Succinic/Sebacic acid (TPU 14) and Succinic/Azelaic acid (TPU 32)) was added to a vial and stirred to homogenization at 75°C. An exothermic reaction is observed and the temperature rose to 150°C. Hexamethylene diisocyanate (6HDI) was added and stirred vigorously. After 5 minutes, the TPU is molded into squares and hardens over 3 days at room temperature.

### 2.3.1 FTIR

TPU 14 and TPU 32 were cut into 2 cm cubes and placed in compost collected from Roger's Community Garden at UCSD in La Jolla, CA at 45degreesC for 3 weeks and 6 weeks. The samples were dissolved in tetrahydrofuran (THF) and subject to vacuum filtration to remove the dirt from the solution. A few drops of the polyurethane solution was set on the FTIR instrument, and a heat gun evaporated the solvent creating a thin film ideal for IR spectroscopy. The sample was scanned 16 times on a Perkin Elmer Spectrum X FTIR spectrometer to output the spectra at a 1 cm-1 resolution.

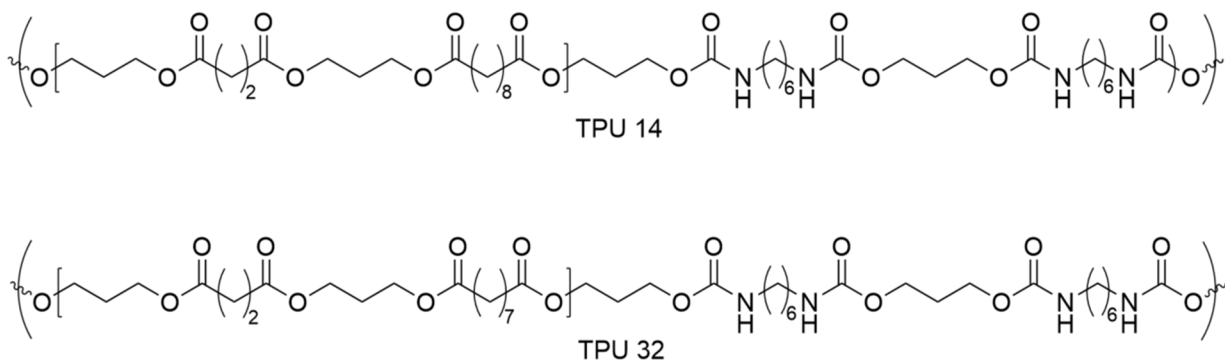


Figure 5: Structures of TPU 14 and TPU 32

### 2.3.2 SEM

TPU 14 and 32 samples were removed from the compost at 9 weeks. The samples were washed with DI water and dried over nitrogen. The samples were cut into 2 mm cubes and adhered to aluminum stubs via carbon tape. Samples were sputter-coated using an Emitech K575X Sputter Coater. The sputter coater deposited a layer of iridium to increase conductivity and image quality. Samples were placed in an FEI Quanta FEG 250 SEM under a high vacuum and analyzed.

## 2.4 Results and Discussion

### 2.4.1 FTIR analysis of compost TPU

The complete FTIR spectra for TPU 14 and 32 are shown in Figures 6 and 7. Important regions of the FTIR spectra for polyurethane degradation analysis are the Amide A, I, II, and III regions and the C-O stretching region of the ester.<sup>19,23,24,28,29</sup>

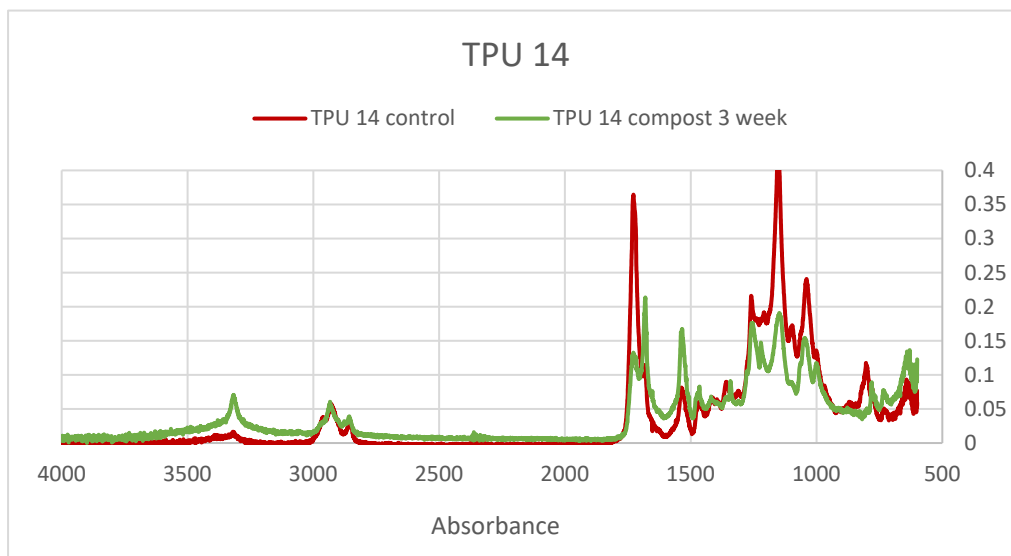


Figure 6: Full FTIR spectrum of TPU 14.

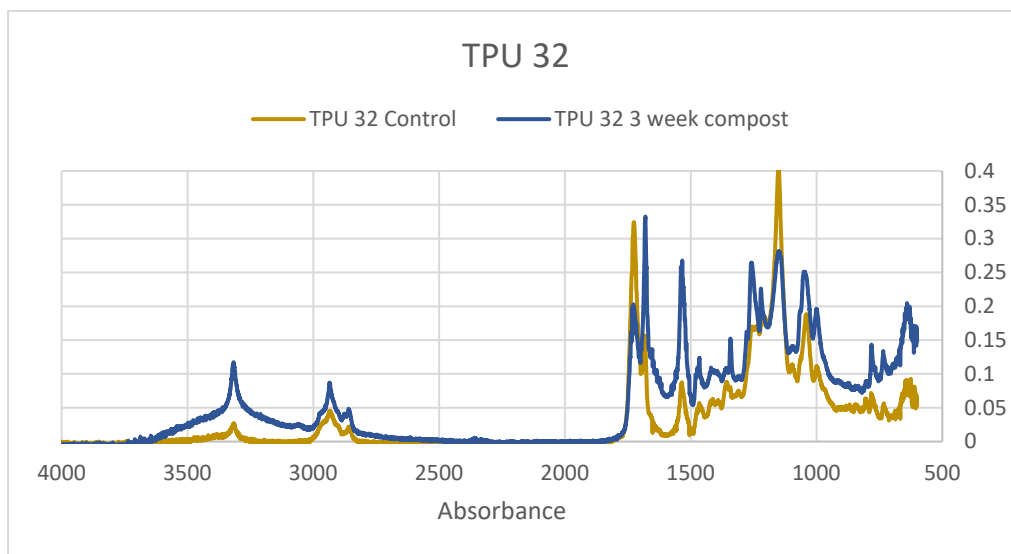


Figure 7: Full FTIR spectrum of TPU 32.

The carbonyl region in control samples TPU 14 and 32 at  $1728\text{ cm}^{-1}$  and  $1725\text{ cm}^{-1}$ , respectively, indicates the presence of both the urethane carbonyl and the ester carbonyl in the soft segment. The broadness of these peaks shows that there must be two different carbonyl bonds because C=O peaks are generally very sharp and distinct. These peaks are also broader than carbonyls in small molecules due to the hydrogen bonding nature of the urethane hard segment. There is another distinct peak in this carbonyl region, which can be identified as the amide carbonyl peak, determined from the lower wavenumber than the ester carbonyl, caused by the delocalization of electrons due to the nature of nitrogen's ability to donate electrons (see fig. 3). Next to the maximum polyester C=O stretch; the amide C=O stretch was identified as  $1680\text{ cm}^{-1}$  and  $1679\text{ cm}^{-1}$ , respectively.<sup>30-38</sup>

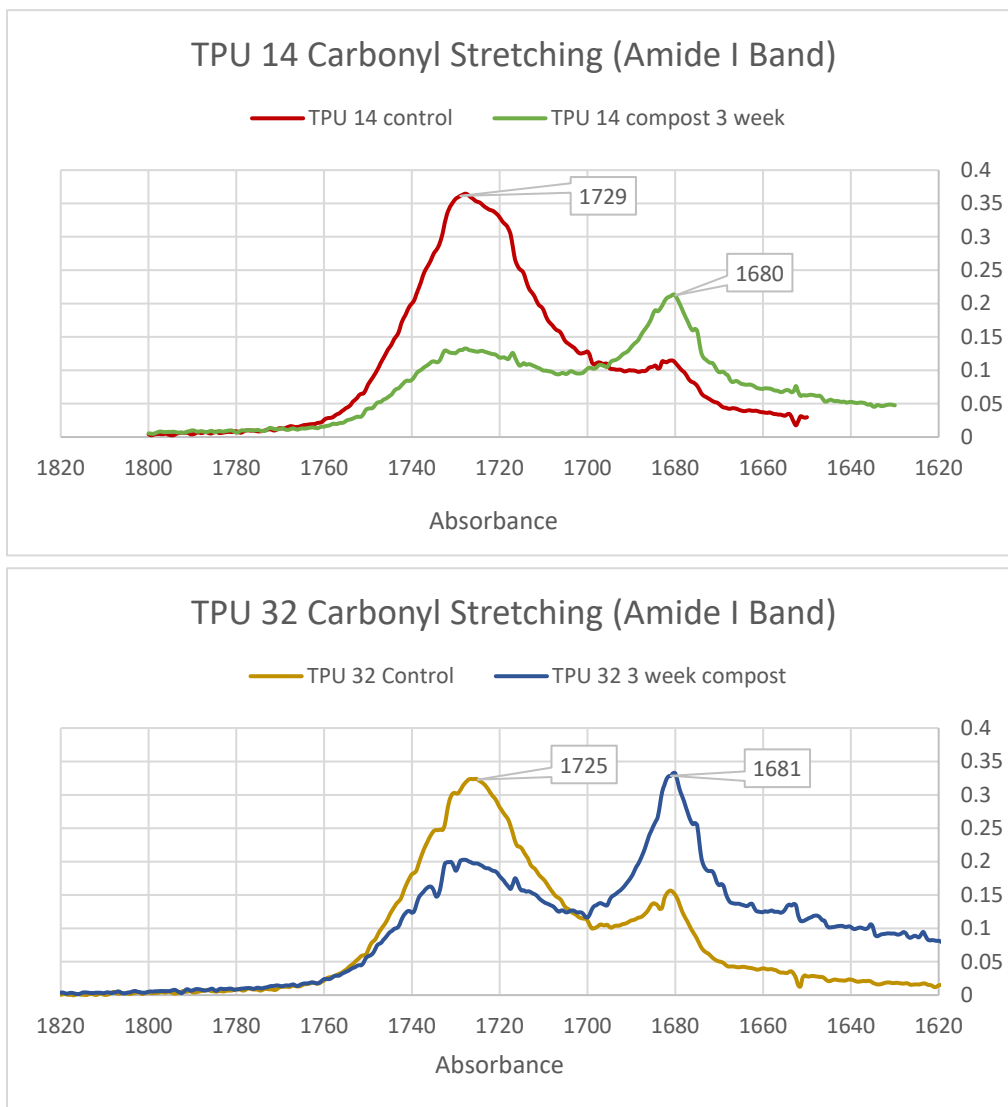


Figure 8: FTIR Spectra of the Amide I Band Region of TPU 14 and 32

In the FTIR spectra of the 3-week degraded PU, the ester carbonyl absorbance is significantly reduced by 62% in TPU 14, and 73% in TPU 32. The amide carbonyl absorbance (Amide I bond) is drastically increased. The ester carbonyl in the soft segment has broken off the polymer chain, and the concentration of hard segment in the TPU has increased. The Amide II and III peaks show further evidence of the urethane moiety degradation. The Amide II bond at  $1534\text{ cm}^{-1}$  has dramatically increased

in the 3-week compost sample of both TPUs, as well as the dramatic decrease of the urethane C-O-C bond at  $1034\text{ cm}^{-1}$  and  $1044\text{ cm}^{-1}$ , respectively.

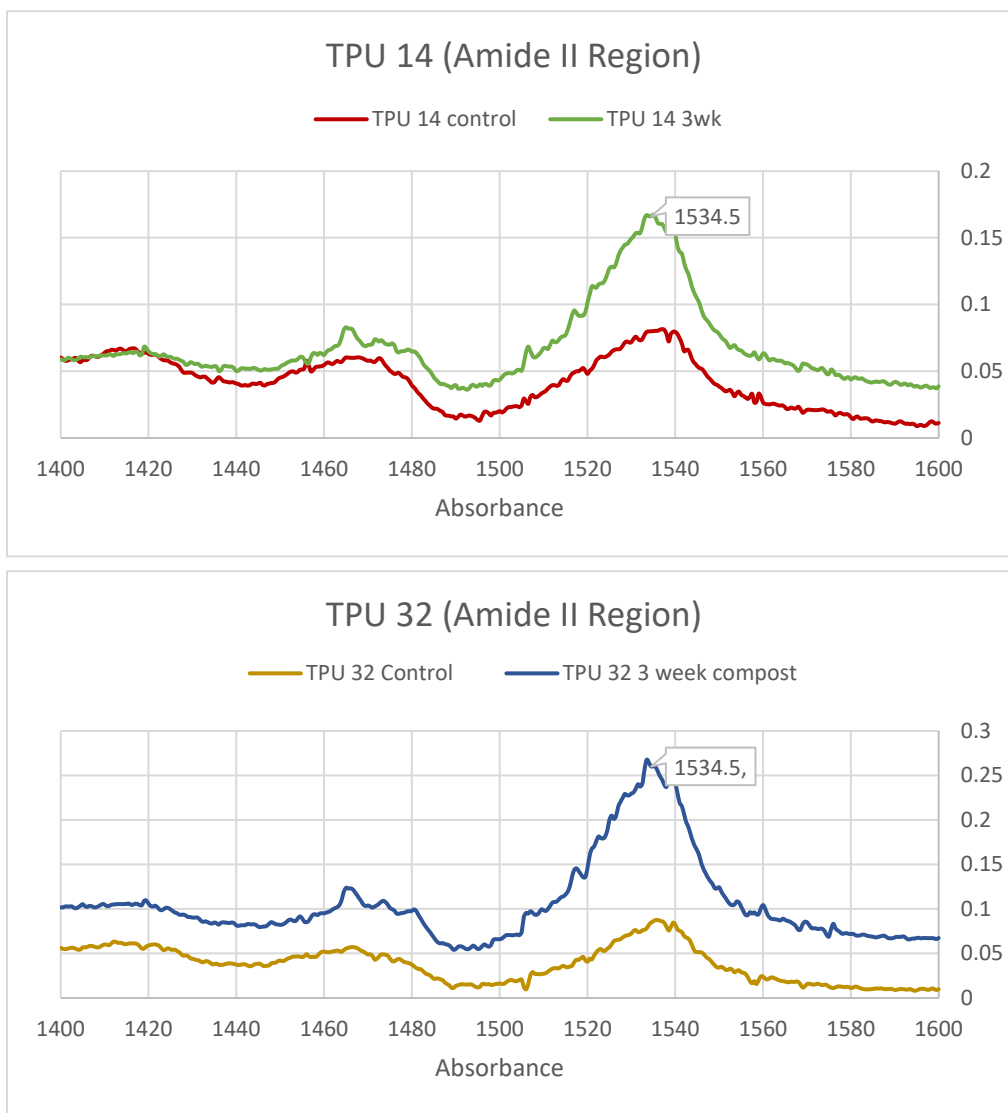


Figure 9: FTIR Spectra of the Amide II Region of TPU 14 and 32

The Amide A bond, representative of the N-H stretching vibration at  $\sim 3316\text{ cm}^{-1}$ , has increased in both samples due to an increase in polarity of the N-H bond in the newly formed amide. This peak is also significantly broadened in the compost sample, indicating that the concentration of non-hydrogen bonded (free) N-H bonds is increasing, which can correlate to the degradation of the crystalline hard segment.<sup>39,40</sup>

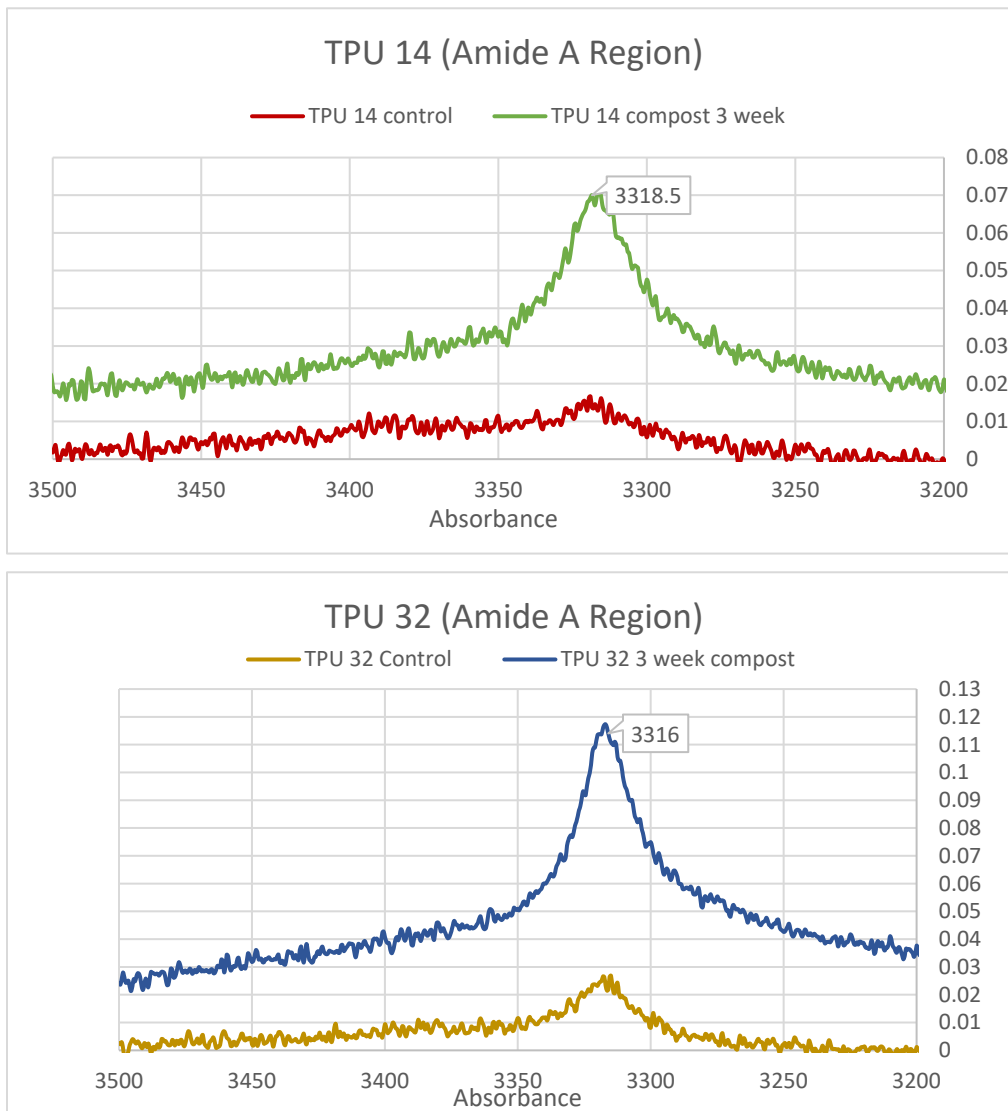


Figure 10: FTIR Spectra of the Amide A Region of TPU 14 and 32

The Amide III band region, around  $1260\text{ cm}^{-1}$  and  $1261\text{ cm}^{-1}$ , respectively, has taken on a similar shape in both samples, representing a general Amide III band with three distinct peaks at  $1277\text{ cm}^{-1}$ , respectively,  $1260\text{ cm}^{-1}$ , and  $1220\text{ cm}^{-1}$ . Because the Amide III region is located within the fingerprint area of the FTIR spectra, it is difficult to analyze with 100% certainty. A complete list of peak identities is shown in Table 1.



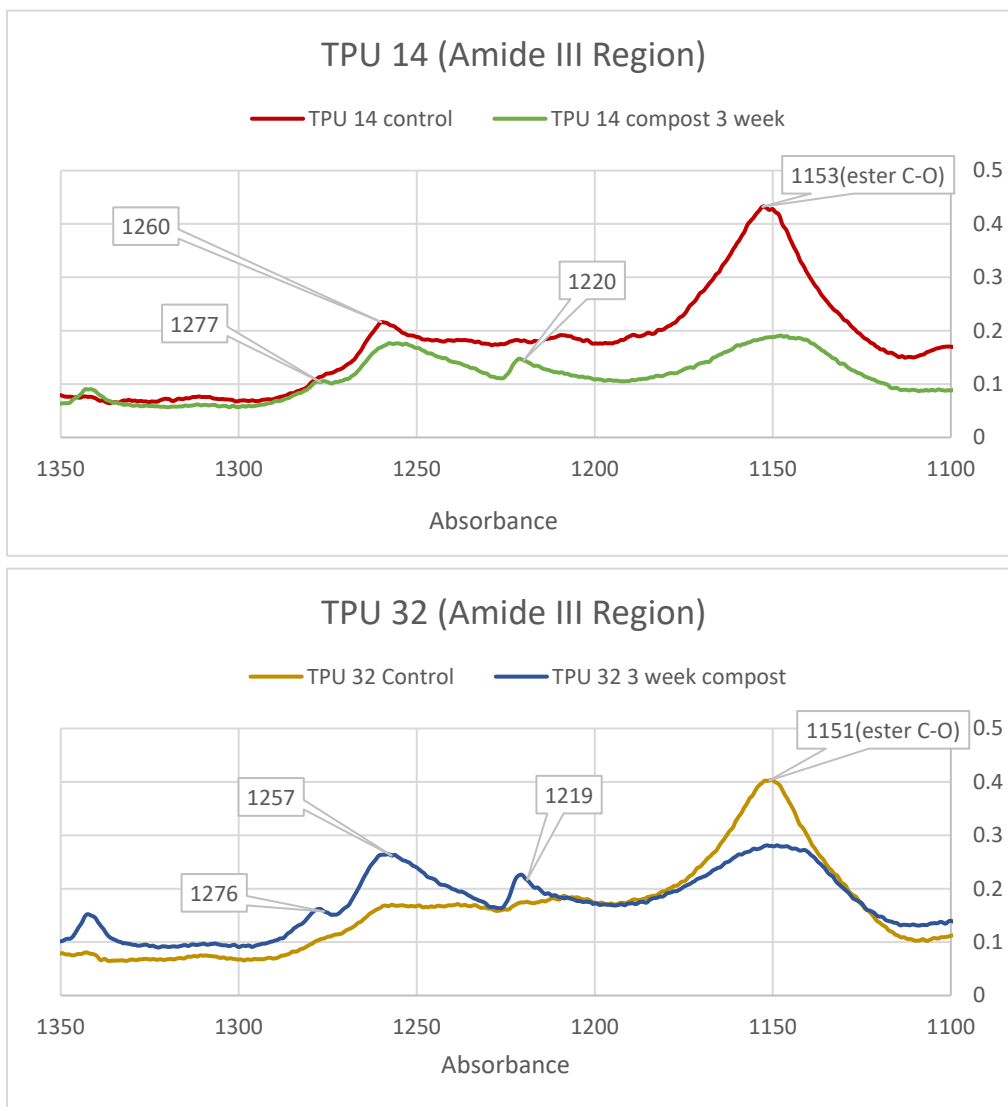


Figure 11: FTIR Spectra of the Amide III region of TPU 14 and 32

Table 1: Peak Identities of TPU 14 and 32

	<b>TPU 14</b>	<b>TPU 32</b>	Notes
Amide A	3318	3315	N-H stretch
Ester C=O	1726	1725	Carbonyl Stretch
Amide C=O	1679	1682	Carbonyl Stretch
Amide II	1534	1534	N-H bending in-plane, C-N and C-C stretching
Amide III	1260	1261	N-H bending in-plane, C-N and C-C stretching
C-O ester	1034	1044	
C-O ester	1153	1153	

#### 2.4.2 SEM analysis of composted TPU

SEM provides a qualitative analysis of the degradation of TPUs. Figure X shows SEM images of TPU 14, control (a), and 9-week compost (b-e). The appearance of cracks, wells, and biological life on the compost sample indicates biodegradation of the polyurethane; the binding of fungal roots and tendrils also indicates that TPU is a carbon source for fungi found in the compost.<sup>21,41-43</sup> Figure 13(e) shows more evidence of fungal biodegradation, where bowl-shaped fungi are seen on the surface of the TPU. The fungus's identity is unclear, and it is assumed the fungus was living in the compost before the experiment. Figure 14 shows SEM images of TPU 32, control (a), and 9-week compost (b-e). In both samples, the integrity of the TPU is compromised, given the appearance of crumbles and deep cracks in the sample.

Images shown in Figures 12 and 13 were published in *J. Appl. Polym. Sci.* 2022, 139(43), e53062

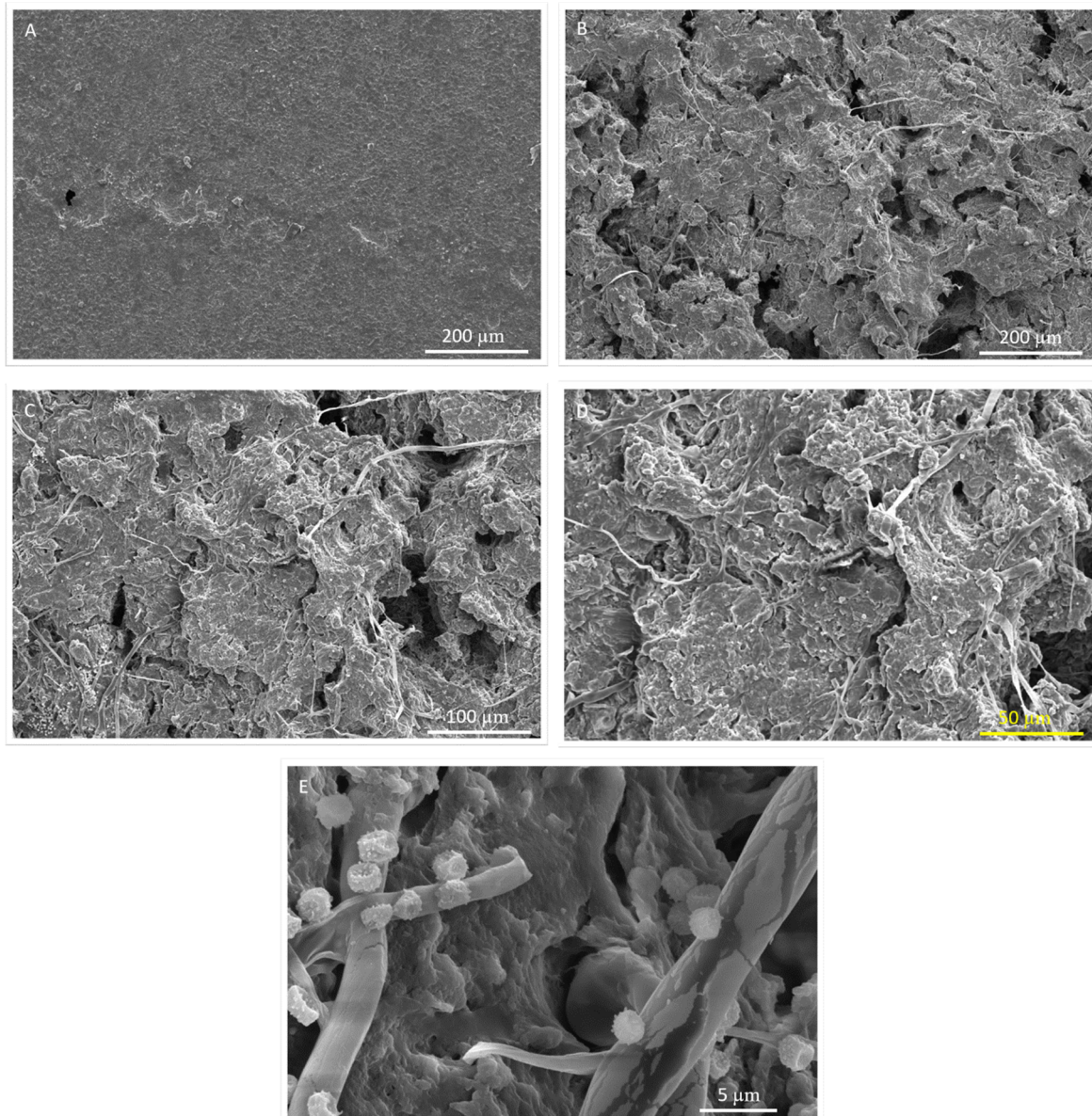


Figure 12: SEM images of TPU 14 A) 0wk B-E) 9wk compost sample

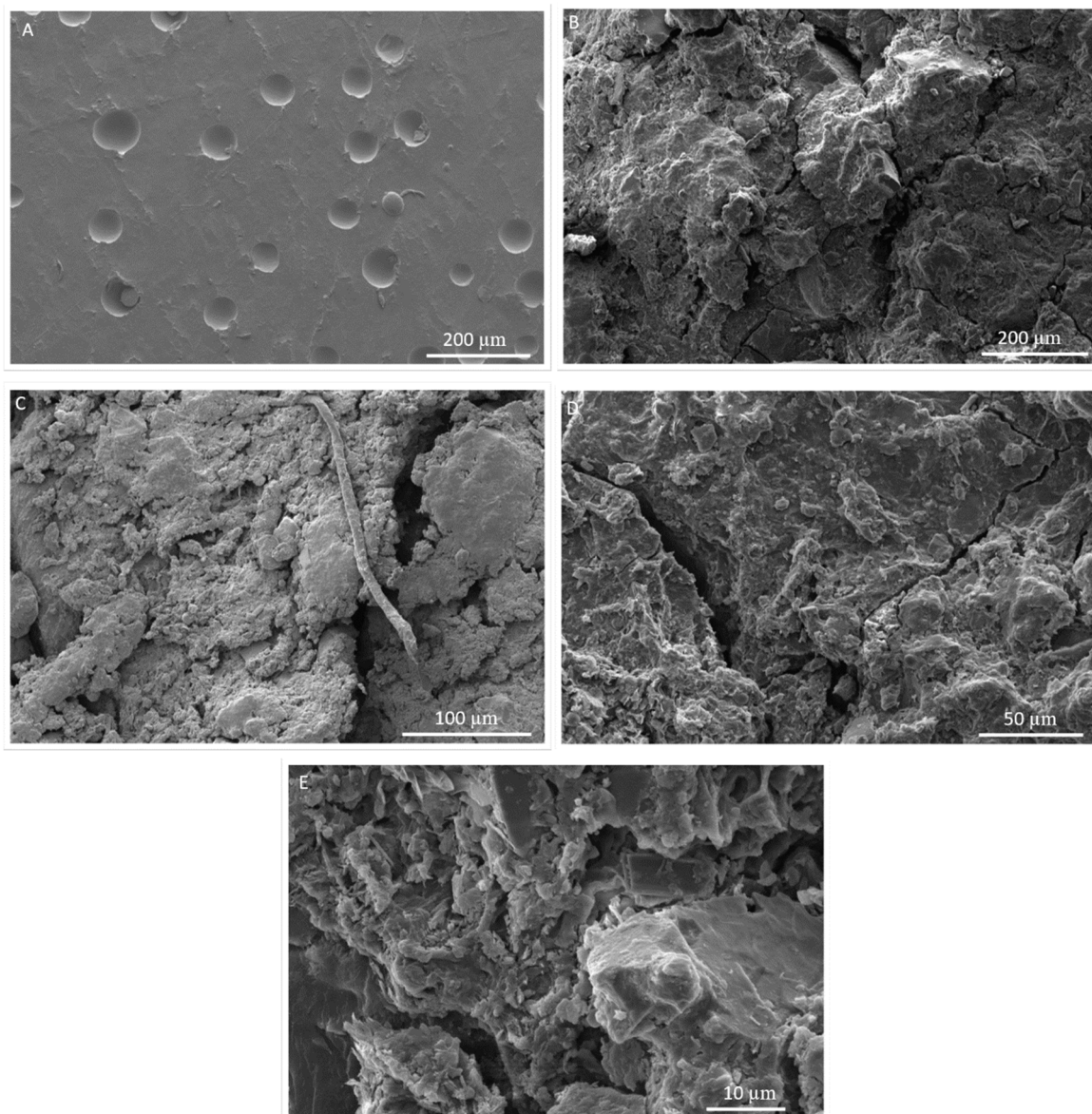


Figure 13: SEM images of TPU 32 A) 0wk B-E) 9 wk compost

## 2.5 Cost-of Analysis

FTIR and SEM are both excellent analytical tools to study the biodegradation of polyurethanes, but the instruments are much different in terms of the time and cost of running samples. FTIR is a fast way to measure functional groups; running one sample takes about 2 minutes. FTIR is the least expensive to obtain compared to other standard analytical equipment such as LCMS or GPC. While this instrument cannot characterize the molecule, it is an excellent instrument in-house.

SEM is a specialty instrument that is much more expensive to purchase and maintain. Operators must also be educated on proper sample prep and machine operation to avoid casualty to the instrument. SEM research is also time-consuming; samples must be dried and sputter-coated before imaging, and analyzing the entire sample can require up to 20 minutes. SEM is expensive - averaging about \$100k for a tabletop model. Comparing FTIR and SEM is not helpful because they do not output the same information.

## 2.6 Conclusion

Two TPU samples were composted at 58°C for three weeks, and the biodegradation was analyzed using FTIR and SEM. The decrease of ester carbonyl stretching at 1729  $\text{cm}^{-1}$  in FTIR analysis indicates the breakdown of the soft segment, while the increase in all three amide bond stretching peak intensities suggests the strong hydrogen-bonded urethane network in the hard segment, which will further be degraded to the parent amine. SEM analysis of the two samples showed microbial life, cracks, and crumbles in the TPU, showing that the structural integrity of a durable TPU has weakened.

## Chapter 3: Analysis of polyurethane biodegradation by *Candida rugosa* using NMR Spectroscopy

### 3.1 Introduction to NMR

Nuclear Magnetic Resonance (NMR) spectroscopy is another analytical technique that can describe a molecule's atomic surroundings and relative positions. The molecular nuclei possess a form of angular momentum called spin, a vector with both magnitude and direction. These spin orientations' energy states degenerate without a magnetic field.<sup>44,45</sup> With a magnetic field present, the spin states split into two energies. When the sample is subject to a constant, strong magnetic field, the molecule can absorb energy from a weaker, nearby magnetic field and produce an electromagnetic signal that can be plotted and analyzed.

Electrons shield the nuclei from the applied magnetic field, and the strength of the shielding electrons is unique to the element, functional group, and position of the nuclei on the molecule. This makes NMR spectroscopy a great analytical tool to characterize chemical structures, monitor the progress of reactions, and determine purity.

<sup>1</sup>H proton NMR analyses hydrogen atoms on the sample. Chemical shifts of hydrogen atoms depend on what the atom is covalently bonded to, as each element contributes differently to the shielding and deshielding of electrons. When the proton is deshielded, the electron density around the hydrogen nuclei is decreased and pulled by neighboring atoms. Neighboring hydrogen nuclei can also affect the magnetic field, known as spin-spin coupling, which splits the signal into two or more lines, indicating how many hydrogen neighbors the nuclei have.

### 3.2 Experimental

TPU 14 and 32 were dosed with 20 U/mL CR enzyme in PBS media on days one and four of the seven-day course. After seven days in enzyme media, the TPU was washed with water and dried before being dissolved in a deuterated solvent in a concentration of 5mg/mL for NMR analysis. 2048 scans were taken on a Jeol ECA 500 NMR for both samples.

### 3.3 Results and Discussion

Full spectra of TPU 14 control and enzymatically degraded are shown in figures 14 and 15.

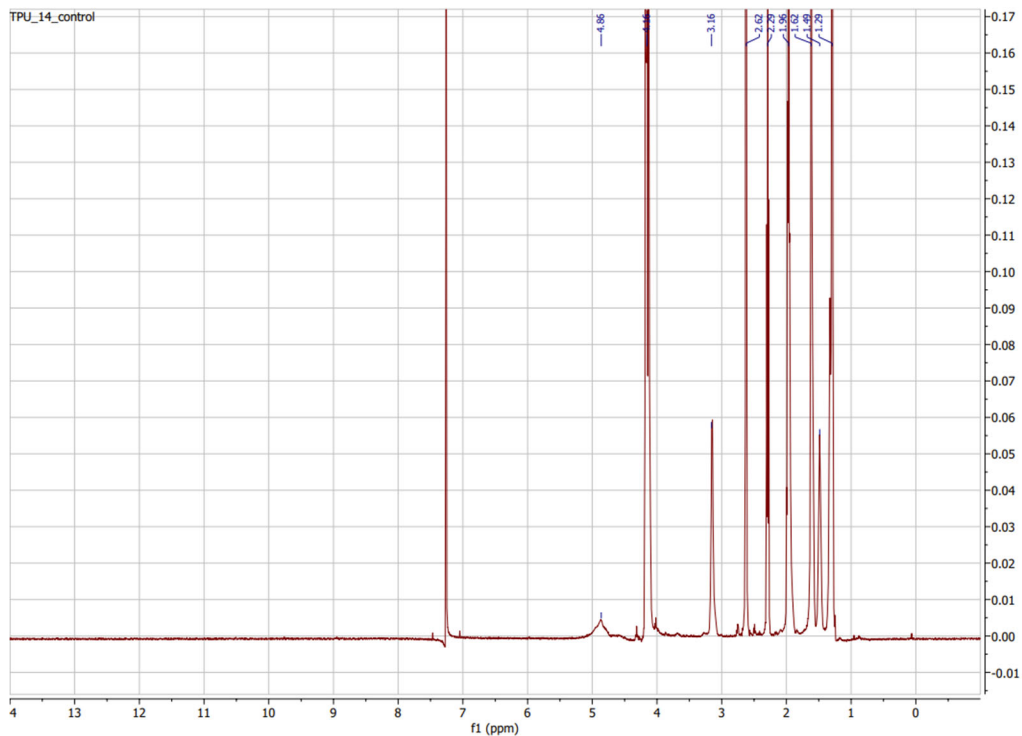


Figure 14: Full NMR spectrum of TPU 14 control sample

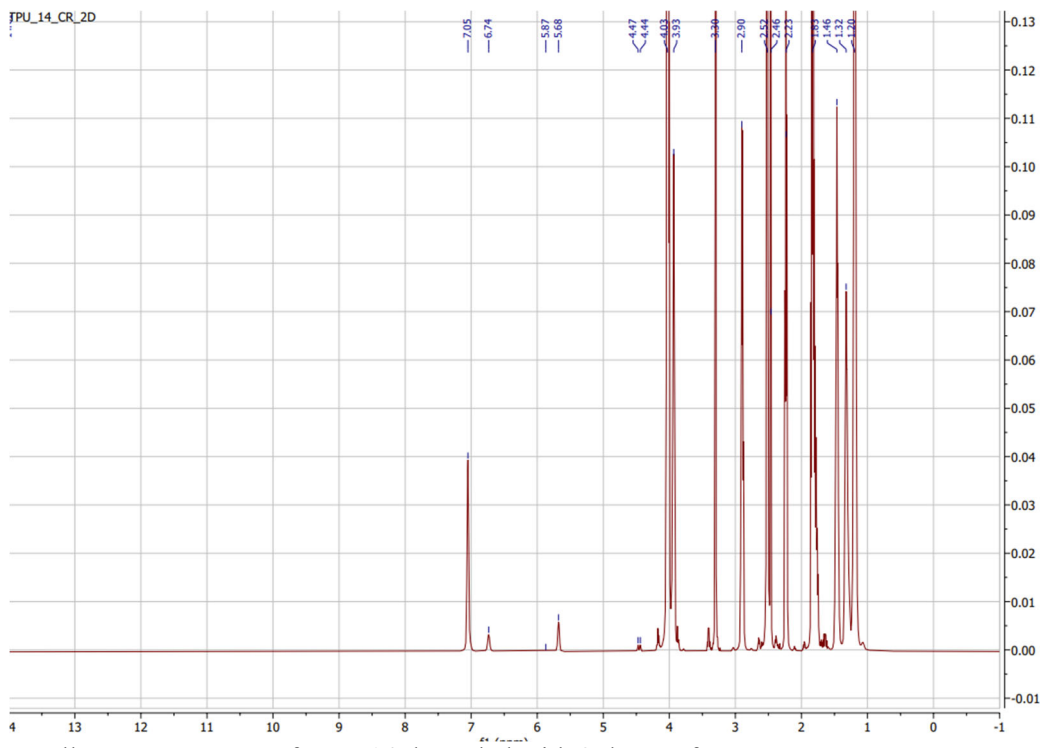


Figure 15: Full NMR spectrum of TPU 14 degraded with 2 doses of enzyme

Peaks at 4.16 (t), 2.28 (t), 1.61 (m), and 1.48 (m) are identified as part of the polyol repeating unit, which retains the same shape in the degraded sample, but has shifted upfield slightly. Analyzing the biodegradation of polyurethanes via NMR spectroscopy can be achieved by looking at the changes in chemical shifts for specific protons, specifically, the N-H nuclei. The N-H nuclei are part of the hard segment urethane (carbamate) group in the original polyurethane, which is a unique, very broad singlet peak at 4.86 ppm. The degraded sample shows new distinct singlets at 7.05, 6.74, and 5.68, indicating a change in the molecular structure of the urethane moiety (Fig. 16). 2D NMR suggests that all three N-H peaks are correlated with a quartet at 2.90 (Fig. 17). It can be theorized that the hydrogen-bond network of ordered urethane bonds is being disrupted, explaining the multiple amide peaks.<sup>38</sup> The ethylene glycol chain extender signals have shifted upfield from 4.13 (t) to 3.93 (t) after enzymatic degradation.<sup>46</sup> The peaks at 4.03, 2.52, and 1.20 ppm are assigned to the soft segment polyol and suggest removal from the long polymer chain. A new singlet at 3.30 is associated with hydroxyl end groups from the breakdown of the soft segment.<sup>16</sup> evidence of the parent amine from 6 HDI is shown by a new triplet at 2.47 ppm and a singlet at 1.20.<sup>47</sup>

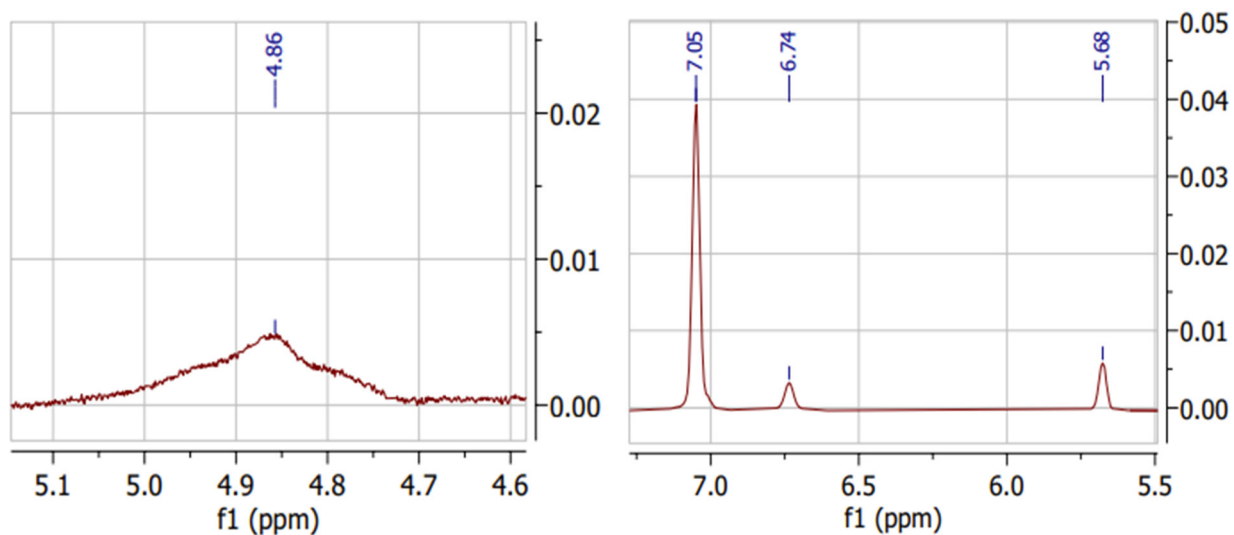


Figure 16: Zoomed images of the N-H chemical shifts in TPU 14 control (left) and TPU 14 enzyme degraded (right)



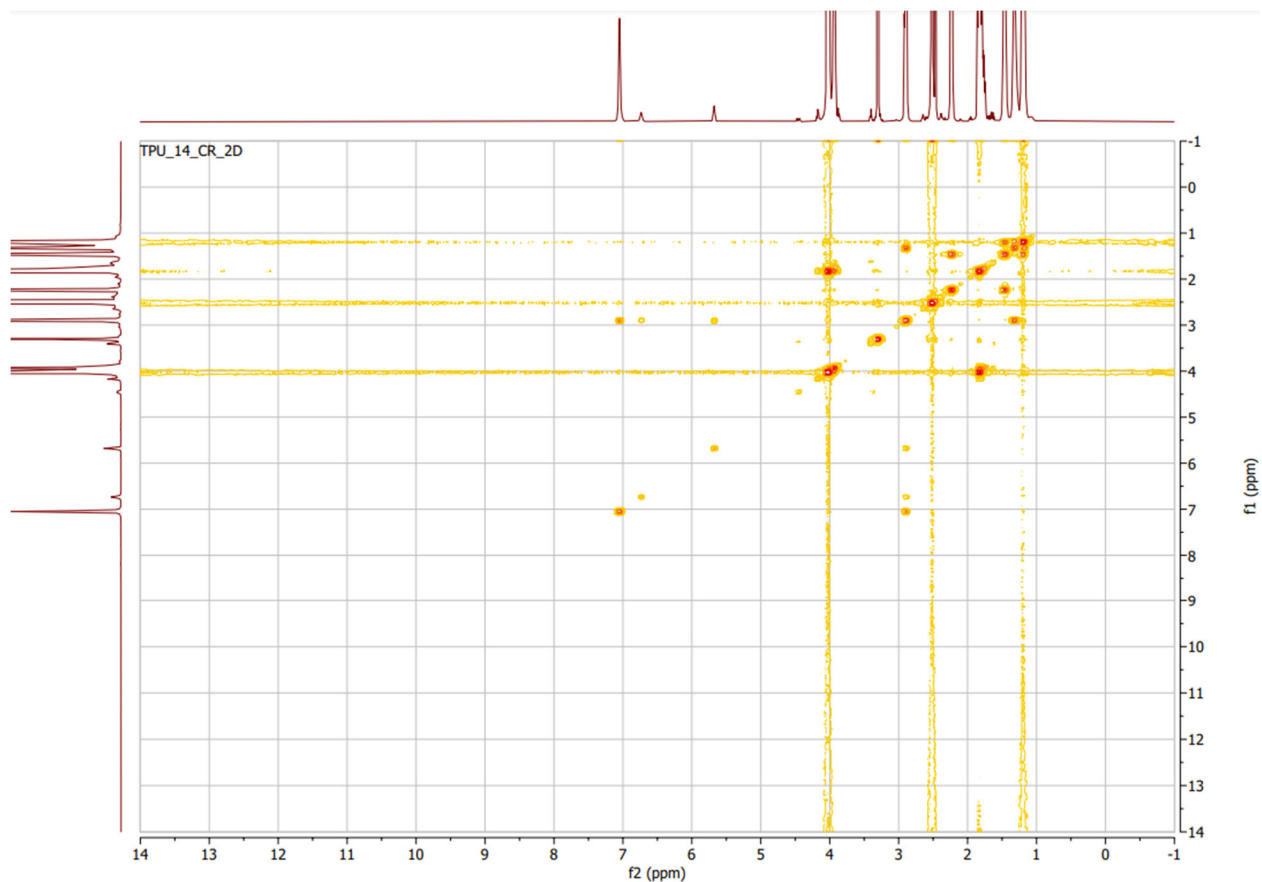


Figure 17: 2D COSY NMR of the enzymatically degraded TPU 14 sample

### 3.4 Cost-of Analysis

NMR is a surefire way to identify a molecule or detect its purity, but the instrument is costly, and it requires a highly skilled technician to oversee its use. Lower-end NMRs start at around \$300,000, while higher-powered NMRs can reach 1 million dollars. To ensure high-quality spectra of polymers, it is recommended to do ~2000 scans which can take up to 30 minutes.

### 3.5 Conclusion

Enzymatic degradation was performed on TPU 14 and analyzed via NMR spectroscopy. The disappearance of the unique urethane N-H peak at 4.86 ppm and the appearance of three different N-H peaks at 7.05, 6.74, and 5.68 ppm indicate degradation of the crystalline urethane structure of the TPU.

Evidence of the parent amine 6 HDI was found in the degraded sample. The peaks at 4.03, 2.52, and 1.20 ppm indicate the breakdown of the soft segment polyol and removal from the long polymer chain. 2D  $^1\text{H}$  NMR was used to correlate peaks in the entire polymer structure of the degraded TPU 14 sample.

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