FORMULATION, EVALUATION, AND BIODEGRADATION PROPERTIES OF FUNCTIONAL POLYURETHANE SYSTEMS BASED ON POLY(1,3-PROPYLENE-1,4-BUTYLENE GLUTARATE)

by

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(Under the Direction of Jason Locklin)

ABSTRACT

In this work, polyurethane systems were explored to assess the feasibility of producing foam and multilayered films that could utilize bio-based monomers and polymers and biodegrade in industrial and home composting environments. Poly(1,3-propylene-1,4-butylene glutarate) (PPBG) polymers were synthesized from monomers that can be bio-sourced. Foam formulations utilizing PPBG and three common isocyanates, Methylenediphenyl-4,4'-diisocyanate (MDI), 2,4-toluene diisocyanate (TDI) and Hexamethylene diisocyanate (HDI), were evaluated for biodegradation in industrial compost concluding that PPBG-HDI based foams show potential for biodegradation while the TDI and MDI based foams don't. Furthermore PPBG-HDI based foams produced exhibited shape memory foam characteristics that were explored using DMA. Isocyanate prepolymers made from PPBG and sebacic acid diisocyanate (SADI) were synthesized and used to adhere polyhydroxyalkanoates (PHA) films to viscose. These films were evaluated for biodegradation in a home composting environment and were found to show promise as a biodegradable multilayered film.

INDEX WORDS: POLYURETHANE, FOAM, ADHESIVE, ISOCYANATE, BIODEGRADATION

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DEDICATION

To my darling wife, whose love and support has meant everything. And to my son who has given us more love and more work than we ever could have imagined.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

Industrial Production of Polyurethanes

Polyurethanes as a class of performance materials have a wide range of uses industrially; medical devices, aerospace, transportation, and consumer goods all utilize polyurethanes' ability to be a thermoplastic, foam, coating or adhesive.[3,7-8] Due to their widespread use, polyurethanes comprise ~8% of all produced plastics in the world.[20] While much work has been done on improving the performance of these materials, comparatively little has been done on the environmental impact on the production and end life of these materials. The majority of polyurethanes are synthesized from petrochemical feedstocks. 4,4-methylene diphenyl diisocyanate (MDI) and 2,4-toluene diisocyanate (TDI) are used the most widely used diisocyanates, they comprise more than 90% of the global diisocyanate market are derived from petroleum sources.[2] Polyisocyanates are typically reacted with an alcohol terminated polymers referred to as polyols, these polyols are generally also petroleum based.[3-4,7-9] The need for sourcing more renewable sources in polyurethanes is only going to grow as petrochemical sources dwindle, prices rise and consumers demand more renewable-based products. Much work has been done on displacing the petrochemical-based polyols in polyurethanes focusing primarily on sourcing plant-based oils and fatty acids. Most of these bio-based fatty acids and oils are large bulky molecules with lower hydroxyl numbers that pose a challenge for the fast kinetics required for foaming polyurethanes industrially.[3-7]

Unfortunately the ultimate endpoint for most consumer goods is the landfill. A 2017 by Geyer and Jambeck determined that the global production of plastic waste was 6.3 billion metric tons.[33] This raises the need for better end of life considerations of polyurethane products. Physical means of recycling polyurethanes are most common but involve using the material as a filler and is only a temporary stop on the way to the landfill. Chemical means of recycling is possible with methods such as glycolysis, but requires strict sorting of flexible and rigid polyurethanes and is very sensitive to impurities, two factors unlikely to be found in postconsumer waste.[17-20] Biodegradation of polyurethanes is an even more attractive option for dealing with postconsumer polyurethane waste, especially since only 9% of plastics are recycled globally.[33] With a biodegradable material, microbes and fungi can digest and break down the materials rendering them biologically innocuous and returning them to the natural carbon cycle. Various studies have identified microbes and fungi can facilitate this in polyester polyurethanes but studies were done under strict conditions not found when in industrial composting or home composting.[10-16] This has raised the strong need to design materials that are bio-based and compostable.

Polyurethane Products

Figure 1.1 Polyurethane foams

Polyurethane Foam Production

The isocyanate-alcohol reaction giving the urethane bond is the main polymerizing reaction in polyurethane foams (Figure 1.2a). This highly exothermic addition reaction releases ~24 kcal per mole of urethane which can be used to further catalyze foaming reactions and volatilize blowing agent. By reacting multifunctional polyols and isocyanates, crosslinked polyurethane matrices can be formed.[8, 21-26] Polyurethane foams consist of an crosslinked polymeric network containing cells of entrapped gas. The gas is introduced to a polyurethane network as it is forming and is referred to as the blowing agent. It can be introduced simply as an element of the formulation (physical blowing agent) or as a byproduct of chemical reactions (chemical blowing agent). Generally polyurethane foams are blown to some degree of the reaction between an isocyanate and water which forms an amine and carbon dioxide, which acts as the blowing agent (Figure 1.2b). While the inert CO_2 acts as a blowing agent, the amine can further react with isocyanates forming a disubstitued urea, further building molecular weight (Figure 1.2c).[8,21-26] The water-isocyanate reaction is also highly exothermic releasing ~47 kcal.[8, 24] Further contributing to the chemical blowing action from the release of CO_2, the heat generated during the exothermic polyurethane and amine reactions can vaporize a portion of the H_2O in a formulation which can also contribute to a foam’s cell formation. At temperatures above 110^{o}C, further crosslinking of the polymer can occur through side reactions. Isocyanates can react with amines forming biurets (Figure 1.2 d) or with polyurethanes forming allophonates (Figure 1.2 e).[8] As the reaction proceeds, viscosity increases dramatically, and the gas can become entrapped in the polyurethane matrix. These voids in the material called cells that give

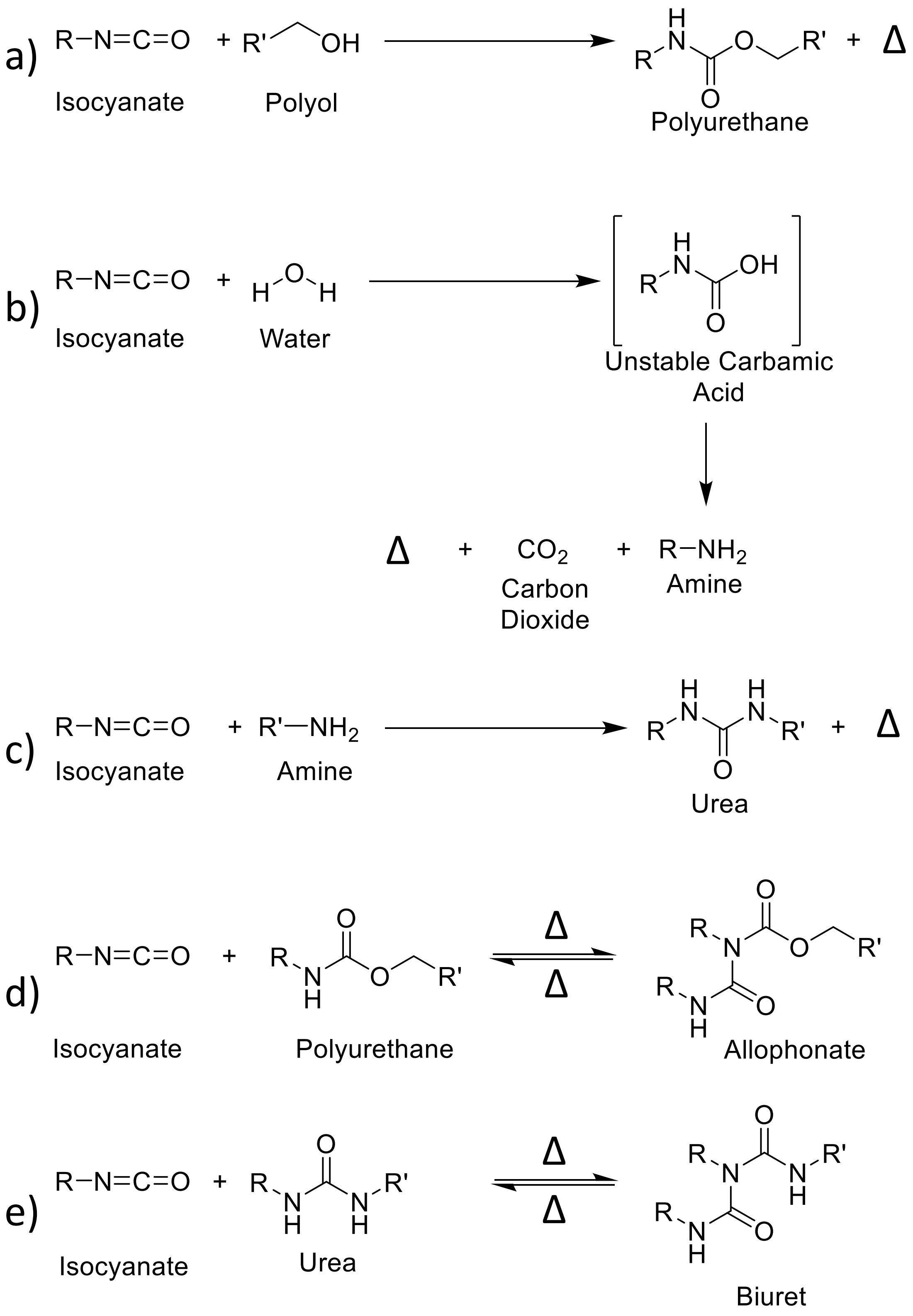

Figure 1.2 a-e. Isocyanate Reactions

polyurethane foams their unique physical structures. Figure 1.3 shows the cells in the interconnected polyurethane network for a typical water blown foam.

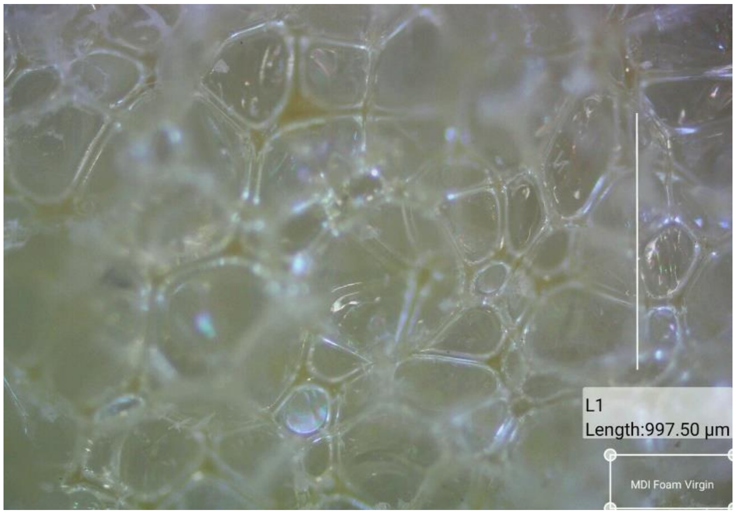

Figure 1.2 Typical cell structure of a water-blown polyurethane foam

Due to the extremely reactive nature of isocyanates, polyurethane foam resins are typically formulated in a two-shot method with isocyanate forming one side of the resin separate from the portion containing the catalysts, surfactants, blowing agents, and reactive polymers (with hydroxyl terminated polymers being referred to as polyols). The ratio of isocyanate end groups to hydroxyl end groups is referred to as a formulation with a ratio of 100 being an equivalent number of isocyanate groups to hydroxyl groups in a formulation. An over index is an index >100 and indicates a larger number of isocyanate end groups to hydroxyl end groups. An under index (index<100) indicates the converse. Foams made at a laboratory scale are typically over indexed at a range of 105-115.

Polyurethane Adhesives

Adhesion is a complex phenomenon involving electrostatic interactions, mechanical interlocking, Van der Waal's interactions, chemical bonding, interchain diffusion.[30-32] One-part polyisocyanate adhesives are widely used industrially and even found in many consumer available glues.[27-32] When used as an adhesive, isocyanates can react with any active hydrogens on a substrate's surface such as hydroxyls (Figure 1.2 a) forming a chemical bond but the primary method of curing and building molecular weight is the water-isocyanate reaction (Figure 1.2 b & c) forming a polyurea. After curing, these systems act as a typical polymeric adhesive with physical crosslinks, chain entanglement, and interactions with the substrate contributing to the adhesion.

Thesis Objectives

The objective of this thesis is to explore the performance and enzymatic biodegradation characteristics of polyurethane with a bio-based polyester in foam formulations and multilayer packaging applications. Foam formulations incorporated either aliphatic hexamethylene diisocyanate (HDI) or aromatic methylenediphenyl-4,4'-diisocyanate (MDI) or aromatic toluene diisocyanate (TDI) and poly(1,3-propylene-1,4-butylene glutarate) (PPBG) polyols. The multilayered systems utilized prepolymers synthesized from PPBG and sebacic acid diisocyanate (SADI). PPBG polyols are able to be synthesized using biologically sourced monomer units. Performance of the foams were evaluated using dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). Enzymatic degradation of the foams and multilayered films were studied using respirometry analysis. After 180 days under industrial composting conditions, the aliphatic PPBG-HDI foams exhibited 84% biodegradation relative to cellulose versus 2% for PPBG-MDI foams and no appreciable biodegradation for PPBG-TDI foams. After 117 days under home composting conditions, multilayer films of polyhydroxyalkanoates (PHA) and viscose adhered with PPBG-SADI biodegraded 42.56% at 20^{o}C and 85.96% at 35^{o}C.

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CHAPTER 2

FORMULATION AND EVALUATION OF POLYURETHANE FOAMS BASED ON POLY(1,3-PROPYLENE-1,4-BUTYLENE GLUTARATE)[1]

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[1] Henkel, T. and Locklin, J. To be submitted to ACS Sustainable Chemistry & Engineering.

Abstract

In this work, a polyurethane foams were formulated using poly(1,3-propylene-1,4-butylene glutarate) (PPBG), a polyester that can be made from bio-based monomers and three isocyanates, Methylenediphenyl-4,4'-diisocyanate (MDI), 2,4-toluene diisocyanate (TDI) and Hexamethylene diisocyanate (HDI). These foams were evaluated for biodegradability in industrial compost using respirometry. Under these conditions, only HDI-PPBG foams exhibited significant degradation. To evaluate the properties of these HDI-PPBG against more traditional MDI based foams as well as commercially available foams, Dynamic Mechanical Analysis was used. It was determined that these HDI-PPBG exhibit memory foam behavior comparable to those on the market indicating that this could be a relevant market for the HDI-PPBG foam.

Introduction

The polyurethane market share as of 2017 was valued at $60.5 billion and growing. Of this market share polyurethane foams make up about 27%.[2-3] Polyurethane foams can be used in a myriad of industries, they have found uses everywhere from energy dampening roles in aerospace, transportation, and shipping to cushioning roles in furniture, mattresses and clothing to acting as insulators in housing and refrigeration. Polyurethane foams have been finding their way into our waste streams in greater and greater numbers due to their pervasive use. The sheer volume of foam produced and introduced into our environment after the end of a foam products life cycle has raised the need to produce foam products that are from more sustainable feedstock and will not persist in our environment.

A huge focus in introducing more biobased material in isocyanates have been on finding alternatives to the petroleum-based polyols. This work has been primarily based on introducing various plant fatty oils and esters, sucrose or cellulose as polyols.[9-12] Poly(1,3-propylene-1,4-butylene glutarate) (PPBG) is an alcohol terminated polyester that can be made from bio-based feedstocks[14-20] and synthesized in an easily scalable manner. In this work, this polymer will be synthesized and incorporated into polyurethane foam formulations.

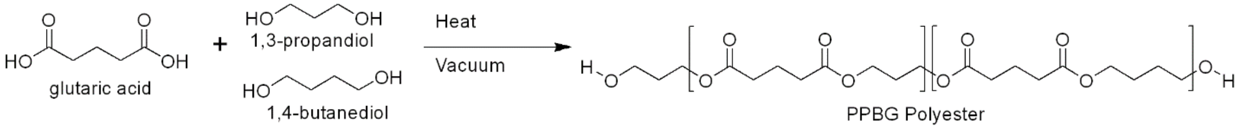

Figure 2.1 Synthesis of linear PPBG Polyester

The urethane bond formed from reacting an alcohol and an alcohol is not a naturally occurring bond. This can prove a challenge when designing a product that will undergo microbial enzymatic degradation as no microbes have evolved specific enzymes for breaking down urethane bonds. Numerous studies have investigated the ability of polyurethane-based foams to undergo biodegradation with a variety of success, but most required specific microbes and not industrially available compost.[44-47] This study will use respirometry to measure the biodegradation of foam formulations containing PPBG and three isocyanates, Methylenediphenyl-4,4'-diisocyanate (MDI), 2,4-toluene diisocyanate (TDI) and Hexamethylene diisocyanate (HDI) in industrial composting conditions. Any foam formulations that show promising results in the compositing study will have the formulations refined and physical properties probed to ascertain if the foam can have any industrial significance.

Experimental Section

Materials

Glutaric acid was purchased from Sigma Aldrich. 1,4-butanediol (BDO) and 1,3-propanediol (PDO) were purchased from Sigma Aldrich. 1,4-Diazabicyclo[2.2.2]octane 2-(DABCO) was purchased from Sigma Aldrich. Bismuth 2-ethylhexanoate was purchased from Alfa Aesar. Dow Corning® 5987 Additive High-efficiency surfactant was provided via sample from Dow Corning®. Triethanol amine was purchased from Sigma Aldrich. Hexamethylene diisocyanate (HDI) was sourced from Acros Organics. Methylenediphenyl-4,4'-diisocyanate (MDI), mixture of di and triisocyanates, was sourced from MilliporeSigma. 2,4-Toluene diisocyanate (TDI) was purchased from TCI

America. Glycerol and pentaerythritol was purchased from Sigma Aldrich. Allswell 3" Memory Foam Mattress Topper Infused with Graphite was purchased from Walmart.

Synthesis of Poly(1,3-propylene-1,4-butylene glutarate) (PPBG)

All PPBG polymers were synthesized via condensation polymerization. Glutaric Acid, BDO and PDO were placed in a 3-neck round bottom flask with stir bar, dean stark and condenser. Reaction was conducted at atmospheric pressure and 165-175^{o}C removing condensed water for 2 hours, if a branched polymer was desired glycerol or pentaerythritol were added and vacuum pulled for up to 48 hours, depending on desired molecular weight. Linear PPBG with a molecular weight of 3648 g/mol was produced at a 500g batch size at 175^{o}C over 41 hours with a molar ration of 0.5mol% glutaric acid, 0.25mol% BDO, and 0.25mol% PDO. A branched PPBG with an average functionality of 3.7 and molecular weight of 8864 g/mol was produced at a 300g batch size at 175^{o}C over 43 hours with a molar ration of 0.5mol% glutaric acid, 0.23mol% BDO, 0.23mol% PDO and 0.02mol% glycerol.

Synthesis of Isocyanate Prepolymers

HDI was diluted to 30% by weight in dry acetone, placed in a round bottom flask under N_2 atmosphere and heated to 60^{o}C. PPBG was diluted to 50% with dry acetone and fed in at ~0.2 mL/min. After full addition of PPBG, reaction was allowed to proceed for addition 5-10 hours. Product was then dried via vacuum distillation.

Production of Isocyanate Foams

Foams were formulated in two shot method with one side comprising of the isocyanate and isocyanate prepolymer and the other side comprised of PPBG polymer, chemical blowing agents, surfactants, catalysts, and crosslinking alcohols. Total batch size for each foam was between 50-100 g. Foams were formulated to have isocyanate indexes to be between 90-110. The polyols, chemical blowing agents, surfactants, catalysts, and crosslinking alcohol were weighed into a 470 mL container and mixed until uniform using a 3-blade overhead stirrer at high rpm. The isocyanate side was weighed directly into the resin and immediately stirred at high rpm for 30 seconds. HDI containing formulations were placed in an oven with indirect heat at 60^{o}C to aid in the isocyanate reactions. Foams were left in oven overnight to finish curing. Foams should be open, semi-closed or closed cell with a density between 0.01-0.1 g/mL.

Characterization of Polymers

Molecular Weight

Molecular weight of PPBG polymers were determined by gel permeation chromatography (GPC). The GPC system consisted of two Shimadzu, LC-20AD pumps, a Shimadzu, SIL-20A automatic sampler, a Shimadzu, CTO-20A column oven, a Shimadzu, SPD-20 A ultraviolet detector, and a Shimadzu RID-10A refractive index detector. The system used chloroform as the mobile phase at a flow rate of 1.0 mL/min, and the molecular weight is reported relative to polystyrene standards.

Hydoxyl Number[21]

Hydroxyl number (OH#) is a measure of the concentration of hydroxyl end groups in a polymer. It was calculated using the following equation.

$$OH\# = \frac{56100 * Polymer\ functionality}{Molecular\ Weight}$$

With the molecular weight being determined by GPC and functionality calculated from monomer feed ratios of the PPBG polymers.

Equivalent Weight[21]

The equivalent weight (eq wt.) of a material is the molecular weight divided by its functionality.

Foam Index[21]

A foam's index is used in formulating. It is a stoichiometric ratio of the number of NCO groups to the number of OH groups in a reaction. For example, if a material has an equal number of NCO groups to OH groups the index would be 100. It is calculated as follows:

$$index = 100 * \frac{\frac{\%wt\ Isocyanate\ A}{eq\ wt. Isocyanate\ A} + \frac{\%wt\ Isocyanate\ B}{eq\ wt. Isocyanate\ B} + \cdots + \frac{\%wt\ Isocyanate\ Z}{eq\ wt. Isocyanate\ Z}}{\frac{\%wt\ water}{eq\ wt. water} + \frac{\%wt\ polyol\ A}{eq\ wt. polyol\ A} + \frac{\%wt\ polyol\ B}{eq\ wt. polyol\ B} + \cdots + \frac{\%wt\ polyol\ Z}{eq\ wt. polyol\ Z}}$$

Characterization of Foams

Dynamic Mechanical Analysis (DMA)

DMA was performed using a TA instruments DMA Q800 V21.3 Build 96 in compression mode. Cylindrical foam samples were used with a thickness of 6-9 mm and a diameter of ~40 mm for frequency sweeps and ~16.5 mm for creep experiments.

Temperature sweeps were performed using 40 mm diameter clamps with a temperature range of -40° to 160°C at 2°C/min at 10 Hz, 0.6% strain and a preload force of 0.1N. A creep mode temperature sweep from 50°-150°C was run with 16mm diameter clamps with a static force of 0.1N a displacement stress of 0.01 MPa, a temperature equilibrating time of 5 mins, displacement time of 15 mins, and a 10°C temperature step.

IR Spectroscopy (FTIR)

IR spectra between 600 and 4000 cm^{-1} was taken using a Thermo-Nicolet model 6700 spectrometer equipped with a Harrick Scientific grazing angle total reflection accessory. Samples were placed on the Ge crystal and secured into place using the included clamp while measurements were taken.

Respirometry

An ECHO respirometer (Slovenske Konjice, Slovenia) was used in this test. 200 mL/min air flow was pumped into each reactor and the composition of exhausted gas was analyzed by the built-in gas sensors. The raw compost used was collected from a 4-5 month old batch from an industrial composting plant located in Athens, Georgia. Forest residue, food waste and livestock manure were generally used as feedstock in this composting plant. Temperature in the composting pile (30 cm depth) was 50°C at the collecting time. The raw compost was sieved using 4.76 mm sieve to make the fine compost inoculum. The Reactor assay consisted of:

- Blank: 250 grams of compost inoculum only, triplicate

- Cellulose (positive control): 250 grams of compost inoculum and 6 grams of cellulose in triplicate
- Polyethylene (PE) (negative control): 250 grams of compost inoculum and 6 gram PE in triplicate
- Sample 1 to 9: 250 grams of compost inoculum and 6 grams of sample in triplicate at 50°C

The respirometer was operated for 180 days. During the operation, the mixture of compost and samples in each reactor was stirred once a week to avoid channeling and control compost moisture. The compost in each reactor was collected for the moisture test right after the stirring. Certain amount of DI water was added in the compost when the compost appeared to be dry. The amount of water used in the rehydration has varied depending on the sample. The total solid, volatile solid, C%, N%, and pH of compost inoculum were analyzed. C% and N% of polymers were analyzed. pH was measured using the method described in ASTM 5338-15. Carbon and Nitrogen content were measured using the method described by Kirsten (1979)[1]. The compost moisture in each reactor during the test was measured by drying 0.2-2.0 g sample in 58°C oven to constant weight (weight change <5%). Biodegradation numbers were produced by monitoring gas flow rate, gas moisture, gas pressure, gas temperature and CO_2 concentration in the gas to calculate the CO_2 evolution (gram) from each reactor. The biodegradation of each sample was calculated by subtracting the average blank compost inoculum CO_2 evolution from the CO_2 evolution of the samples and then being divided by ideal CO_2 evolution from each sample. All samples in triplicate were averaged together.

Results and Discussion

1. Foam Formulation

Creating a foam product requires a balancing act between building molecular weight at a rate fast enough to support the structure of a foam as it rises and forms a network of cells around the physical and chemical blowing agents and slow enough that the viscosity does not increase to a point that in inhibits cell formation and ability for the foam to rise. Due to the nature of the initial rapid high sheer mixing of the foam components, all components must be either liquid or dissolved solids.

The main polymer chosen to react with the isocyanates was Poly(1,3-propylene-1,4-butylene glutarate) (PPBG), an alcohol terminated polyester synthesized through condensation polymerization with glutaric acid, 1,4-butanediol (BDO) and 1,3-propanediol (PDO). Vinogradova and Korshak noted in their studies that melting point and viscosity of a polymer can be lowered by interrupting the stereochemical regularity of a polymer chain.[48] This lowers the ability of the chains to pack in tightly and align for the dipole-dipole interactions of the carbonyls thereby lowering the interchain reactions between polymer chains and depressing the viscosity of the polymers. By copolymerizing 1,4-butanediol and 1,3-propanediol with glutaric acid (Figure 2.1), liquid polymers down at room temperature with the molecular weight ranges used in this study were synthesized. Subsequent polymerization of glutaric acid with 1,4-butanediol alone and 1,3-propanediol alone yielded polymers that were solids with melting points in the range of 60^{o}C-70^{o}C. Branching was introduced to polymers by glycerol, a naturally occurring triol found in triglycerides found in plant and animal fat[20], or using pentaerythritol. PPBG can be made catalyst free achieving molecular weights in the range of 1,000-15,000 g/mol at 180°C while pulling a vacuum with a reaction time ranging 30-72 hours, this bodes very well for a scalable, industrially friendly reaction. Glutaric acid, 1,4-butanediol and 1,3-propanediol have all been shown to either be industrially produced from renewable sources or can potentially be bio-based[14-19] meaning PPBG can be a 100% bio-based polymer component decreasing the environmental impact of the foams produced. This polymer contributes 24-32wt% of the total foam formulation. GPC for PPBG polymers used can be found in Appendix B.

Choice of catalysts, blowing agents and crosslinking agents were limited to components that would not impact the health of enzymes or microbes that would break down and biodegrade the end foam products. To promote the urethane forming (gelation) reaction between polyol and isocyanate, organometallic catalysts are used. The organometallic catalysts act as a Lewis acid forming activated complexes with the isocyanate and polyol components.[21-23] Tin complexes are the most commonly used organometallic catalysts in industry[4,5,21] but have high cytotoxicity. These tin catalysts can not only impact human health in consumer goods but can completely kill off soil and compost flora rendering it completely inert and unable to undergo any enzymatic or microbial degradation processes.[4-5] Bismuth 2-ethylhexanoate, an alternative to the tin catalysts, was chosen to be the primary gelation catalyst. Bismuth catalysts have been shown to have comparatively low toxicity[4-5] and thus have a low risk of impacting compost health and thus more likely to allow systems to biodegrade. Tertiary amines are just as widely used industrially in foam production to promote the water-isocyanate (blow) reaction as well as contribute to the gelation reaction.[2,3,21] A proposed mechanism for this reaction involves the tertiary amines' lone pair of electrons on the nitrogen forming complexes with isocyanates via a nucleophilic attack on the isocyanate group's carbon. From this complex the nitrogen in the isocyanate group can readily react with any hydrogens from any water or hydroxyls.[21] Due to their low vapor pressure, many amine catalysts can off gas after the foam has reacted giving unpleasant odors and posing serious health complications.[25] The catalytic amines used in this study were chosen to avoid these issues. 1,4-diazabicyclo (2,2,2)octane (DABCO) and triethanolamine were the amine catalysts selected for this study. Triethanol amine, widely used in the pharmaceutical and cosmetic industry, has a low toxicity[26] and has the benefit of also acting as a crosslinking agent due to the three free hydroxyls available for the urethane reaction, this chemically binds the amine into the polymeric network minimizing any chance for off gassing resulting in unpleasant odors or impacting compost health. DABCO is a diamine solid that has low toxicity and a high vapor pressure[24], these properties make any off gassing or compost poisoning unlikely. Glycerol was used directly in formulations as a crosslinking agent.

Polymeric diphenylmethane diisocyanate (MDI) and 2,4-toluene diisocyanate (TDI) are the most commonly used isocyanates in the polyurethane market[2-3,21-23]. These

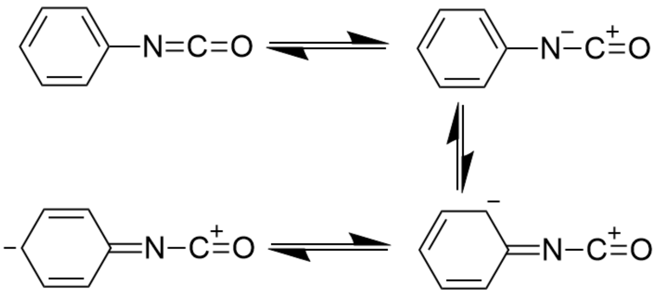

Figure 2.2 Resonance forms of aromatic isocyanate

isocyanates are prized in industry due their high reactivity.[6-8,21-23] Resonance forms from the aromatic isocyanates lower electron density on the -NCO isocyanate group. This in turn make the -NCO group more active in nucleophilic attacks (Figure 2.2) versus aliphatic isocyanates such as hexamethylene diisocyanate (HDI). By introducing an aromatic substituted isocyanate, the relative reaction rate of the isocyanates can be several orders of magnitude higher than a comparable aliphatic isocyanate.[6-8] Urethane bonds also benefit enhanced stability from aromatic resonance from urethanes formed with PMDI or TDI.[27,28] Foam formulations utilizing TDI, MDI, and HDI, representing two aromatic and one aliphatic isocyanate were submitted for respirometry to evaluate the biodegradation potential of these foams under an industrial composting environment. Formulations were kept as close as possible to each other while accommodating the differing reactivity of PMDI, TDI, and HDI. Due to their higher reactivity, PMDI and TDI based foams were made with a conventional two pot method wherein the isocyanate comprises one side of the formulation and is mixed into the resin containing the polyols, surfactants, crosslinkers and catalysts.[21] The comparably low reactivity of HDI required a

Table 2.1 Typical Aromatic Isocyanate Foam Formulation

	Component	Molecular Weight (g/mol)	Hydroxyl Number	Functionality	Weight %	Mass (g)
Part A Resin	Water	18.0	6234.4	2.0	3.0	1.5
	DOW 5987	-	335.1	-	2.0	1.0
	Bismuth 2-ethylhexanoate	638.6	-	-	0.3	0.2
	Polyglutarate 01-47	6909.0	16.2	2.0	5.0	2.5
	Polyglutarate 01-94	1816.0	160.7	5.2	12.6	6.3
	DABCO 30% in ethylene glycol	71.7	1268.3	1.6	1.3	0.6
	Triethanolamine	149.2	1128.3	3.0	6.0	3.0
Part B Isocyanate	MDI	278.6	32.3	2.1	69.7	34.9

modified approach for formulating foams utilizing the aliphatic HDI. A typical formulation for aromatic MDI (Table 1.1) resulted in a top of rise of 2 minutes 20 seconds, the same formulation with same indexing utilizing the aliphatic HDI was still unreacted 1 hour after mixing at ambient temperature. Adjusting the concentration of catalysts, crosslinkers, blowing agents, surfactants, or index as well as increasing or decreasing polyol branching or molecular weight resulted in foams that either blew apart, collapsed, or remained unreacted at room temperature. In the case of the foams that blew apart, the molecular weight was not able to increase the viscosity high enough to support the foam and capture the blowing agents as they were chemically produced or vaporized forming cells, resulting in a collapse of the foam. To aid in building molecular weight and viscosity quicker, isocyanate prepolymers using the Poly(1,3-propylene-1,4-butylene glutarate) (PPBG) and HDI were synthesized. Many studies have explored the production of isocyanate prepolymers and concluded that various polymers can be end capped with isocyanate without crosslinking by tightly controlling stoichiometry with an excess of isocyanate and slowly feeding in the polyol.[27-32] PPBG with a molecular weight of 1816 g/mol and a functionality of 5.2 was fed into an excess of HDI resulting in 3.7mol% isocyanate prepolymer in free HDI (Figure 2.3). The free HDI was desirable

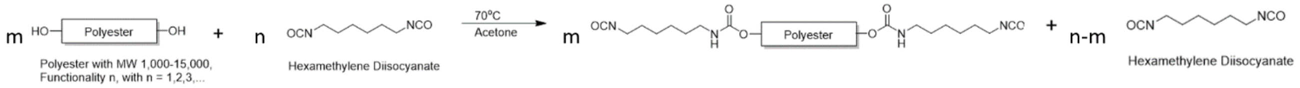

Figure 2.3 Synthesis of isocyanate prepolymer

for the foam reactions as it decreased the viscosity of the prepolymer and increased the concentration of free isocyanate groups available for the foaming reactions. Formation of the urethane bond while preserving isocyanate functionality was confirmed via NMR of the prepolymers (Figure A2). The N-H bond in the urethane bond can be seen appearing at 7.1 ppm, downfield of the C-H bonds in PPBG and HDI from 1.5-4.5ppm. Table 1.2 outlines a HDI and HDI prepolymer formulation that resulted in a robust foam due to the foam being placed in the oven after mixing, top of cup and top of rise times were missed. After mixing, the foam mixture was placed in an oven at 60°C and allowed to rise and cure overnight at elevated temperature to aid in the reactions. The HDI foam in Table 1.2 can be 37% bio-based, taking into consideration the PPBG portion of the foam.

Table 2.2 Typical HDI foam formulation, 50g batch size

	Component	**Molecular Weight (g/mol)**	**Hydroxyl Number**	**Functionality**	**Weight %**	**Mass (g)**
Part A Resin	Water	18.0	6234.4	2.0	3.0	1.5
	DOW 5987	-	335.1	-	2.0	1.0
	Bismuth 2-ethylhexanoate	638.6	-	-	0.3	0.2
	Polyglutarate 01-47	6909.0	16.2	2.0	5.0	2.5
	Polyglutarate 01-94	1816.0	160.7	5.2	12.6	6.3
	DABCO 30% in ethylene glycol	71.7	1268.3	1.6	1.3	0.6
	Triethanolamine	149.2	1128.3	3.0	6.0	3.0
Part B Isocyanate	Isocyanate Prepolymer 01-95	278.6	32.3	2.1	69.7	34.9

Synthesis of PPBG is a robust catalyst free reaction and should have no issues with production at scale. Cohesive foam products using synthesized PPBG, and a variety of isocyanates were produced. To combat aliphatic HDI's lower reactivity, prepolymers with PPBG were synthesized and successfully formulated into a cohesive foam.

2. Biodegradation of Foams

Respirometry was performed on samples of 180 days at 50^{o}C to replicate industrial composting. In order to ensure foams will be starting from the same level for respirometry and not have differing catalyst levels that could affect microbe activity, Table 2.3 shows the formulations used for respirometry testing. These formulations resulted in foams that were semi-closed with a density of 0.056g/mL for MDI based and 0.12 g/mL for TDI. The HDI formulation collapsed on itself after mixing. This occurs when the urethane forming gelation reaction between polyol and isocyanate is not able to build molecular weight and viscosity quick enough to form a strong enough network to trap the CO_2 gas released from the reaction between water and isocyanate as well as the water vaporized from the exothermic nature of the reaction. While this would not be a useable foam product, the isocyanate fully reacted with the water and polyols, confirmed by IR, and from a chemical perspective there is no difference between a foam and a

Table 2.3 Foam formulations for respirometry analysis

Component		**Molecular Weight (g/mol)**	**Functionality**	**Weight % MDI Foam**	**Weight % TDI Foam**	**Weight % HDI Foam**
Part A Resin	Water	18	2	1.6	1.9	1.9
	DOW 5987	-	-	0.5	0.6	0.6
	Bismuth 2-ethylhexanoate	638.6	-	0.8	1.1	0.9
	DABCO 30% in Water	24.173	2	0.3	0.3	0.3
	Glycerol	92.09		2.6	3.1	3.1
	Polyglutarate 01-67	2486	2.3	39.4	46.0	46.7
	Polyglutarate 01-68	2498	4.5	7.9	9.3	9.4
Part B Isocyanate	Hexamethylene diisocyanate (HDI)	168.2	2			
	2,4-Toluene diisocyanate (TDI)	174.2	2		37.8	
	Methylenediphenyl-4,4'-diisocyanate (MDI)	283.786	2.3	46.8		37.1
			Index	**110**	**110**	**110**

collapsed foam, the chemical bonds formed are the same. The difference is purely in the lack of the physical cells in the product's structure. For the purposes of a comparison of the biodegradation ability of the chemical bonds in the aliphatic HDI formulation versus the aromatic MDI and TDI formulations, a collapsed foam would not have any effect on the chemical bonds present. In addition, during preparation for respirometry samples are cryoground into smaller particles and any differences in foam structure is lost. Figure 2.5 shows the absolute biodegradation of the MDI, TDI and HDI foam formulations.

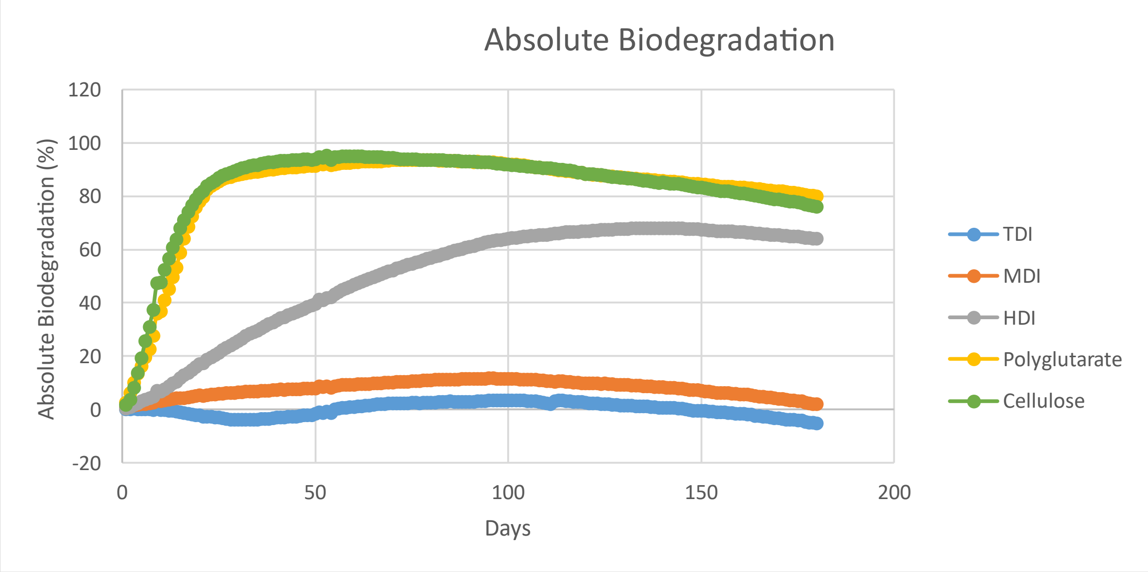

Figure 2.4 Absolute Biodegradation results for polyurethane foams

Cellulose was added as a positive control. Cellulose is used as a blank because it is the most common naturally occur polymer and readily biodegrades. PPBG used in the formulation was added in as well. Absolute biodegradation results can be seen in Table 2.4. PPBG can be seen to be biodegrading at the same rate or faster than cellulose during the entire time frame ending at 79.94% absolute biodegradation versus 75.94% for cellulose. This is expected as PPBG is a polyester with a melting point close to the study temperature and ester bonds are well known to readily degrade. TDI and MDI samples show very little to no biodegradation over 180 days ending at -5.30% for the TDI formulation and 1.86% for the MDI formulations. The HDI formulation shows promising results ending at 64% absolute biodegradation. It was not unexpected that the HDI formulation would achieve a higher biodegradation rate than the aromatic polyurethanes as the urethane linkages benefit from additional stability from resonance into the adjacent aromatics.

Table 2.4 Absolute biodegradation results

Sample	**Absolute Biodegradation**
Cellulose	75.94
TDI	-5.30
MDI	1.86
HDI	64.00
Polyglutarate	79.94

This respirometry study indicate HDI based foams will vastly outperform PMDI and TDI based foams in an industrial composting environment. Further focus of the work will be on HDI based systems as this could result in a high performing foam that can be industrially composted at end of life of any products it is incorporated into.

3. Foam Performance

In addition to their high reactivity, aromatic isocyanates have been prized for the mechanical properties they give when incorporated into polyurethanes.[21-23,31] Polyurethanes are block copolymers consisting of hard urethane segments and the flexible polymer chains. The aromatics in MDI increase the urethane hard segments even further adding to the rigidity of materials made from them.[23,31] Respirometry results indicate that foams based on MDI-PPBG show nominal biodegradation in industrial composting settings while the HDI foams show promising biodegradation results. To evaluate the usefulness and performance of HDI based foams, the effect of increasing HDI content on a foam's viscoelastic property was probed. Three foam formulations with PPBG (Table 2.5) were produced utilizing 100% MDI, 100% HDI, and 50% MDI, 50% HDI. Formulations differed slightly in polyol selection due to polyol availability and foam cohesion but were kept as close as possible while still forming a functional foam. 100% HDI foams required synthesizing prepolymers to be used on the isocyanate side of foam formulations to form workable foams. These three foams were then analyzed via Dynamic Mechanical Resonance (DMA). DMA techniques probe a

Table 2.5 Isocyanate foams produced for DMA testing

	Component	**Molecular Weight (g/mol)**	**Functionality**	**Wt % MDI Foam**	**Wt % HDI-MDI Foam**	**Wt % HDI Foam**
Part A Resin	Water	18.0	2.0	1.8	2.6	3.0
	DOW 5987	-	-	1.4	1.8	2.0
	Bismuth 2-ethylhexanoate	638.6	-	0.1	0.2	0.3
	DABCO 30% in ethylene glycol	71.7	1.6			1.3
	DABCO 30% in Water	24.173	2	0.8		
	Triethanolamine	149.2	3.0		1.8	6.0
	Glycerol	92.09		5.4	3.5	
	Polyglutarate 01-47	6909.0	2.0	8.2	8.8	5.0
	Polyglutarate 01-94	1816.0	5.2			12.6
	Polyglutarate 01-67	2486	2.3	4.1	5.3	
	Polyglutarate 01-68	2498	4.5	12.2	17.7	
Part B Isocyanate	Isocyanate Prepolymer 01-95	278.6	2.1			69.7
	Hexamethylene diisocyanate (HDI)	168.2	2.0		23.0	
	Methylenediphenyl-4,4'-diisocyanate (MDI)	283.786	2.256	66.0	34.3	
			Index	**110**	**105**	**100**

material's viscoelastic properties by applying sinusoidal stress and measuring the resulting strain. Storage modulus (E') is a measure of the elastic response of a material and is directly proportional to the stiffness of a material, the loss modulus (E'') is indicative of energy lost to heat due to internal motion and relaxation, and tan δ is a ratio of E" to E'. Peaks in the tan δ are indicative of the glass transition temperature (T_g).[36-38]

The block copolymers produced in the urethane-PPBG foams consisted of hard urethane segments and the flexible polymer chains. Cross linking agents such as glycerol can increase the hard segments even further. These soft and hard segments can experience separate glass transitions (T_g) and other separate relaxation events in the same

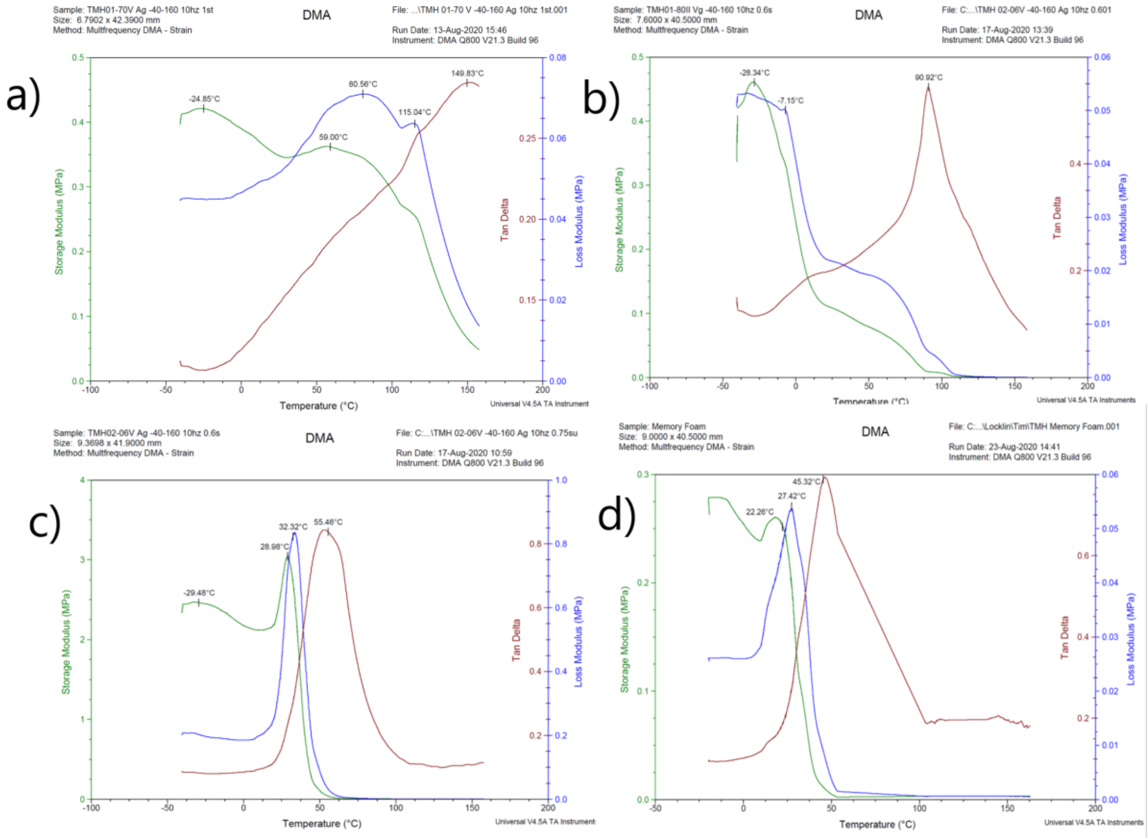

Figure 2.5 DMA temperature sweep results for a) MDI-PPBG foam, b) 50% MDI, 50% HDI-PPBG, c) HDI-PPBG and d) commercially available memory foam

polymer.[33-35] Figure 2.5 a)-c) shows the DMA curve for the PPBG foams. All three foams see maxima in the storage modulus around -25° to -30°C. The MDI-PPBG foam sees a second maxima at 59.0°C, the HDI-PPBG sees a second maxima at 28.98°C and the 50% MDI, 50% HDI-PPBG foams exhibit no second maxima. Since the main difference between these foams is the isocyanate used, it can be hypothesized that the transition around -25° to -30°C is associated with some relaxation event occurring in the PPBG block of the polymer. The maxima at 59.0°C in the MDI-PPBG sample is likely associated with relaxation events in the aromatic polyurethane blocks and the 28.98°C maxima in the HDI-PPBG sample is likely associated with relaxation events in the aliphatic polyurethane blocks. The 50% MDI, 50% HDI-PPBG sample exhibits no second peak, but some shouldering in the 25°-80°C indicating there may be some relaxation events occurring, but further investigation is necessary. The storage modulus is directly proportional to the stiffness, the higher the storage modulus, the stiffer the material.[36-38] The MDI-PPBG foam had a maximum storage modulus of 0.43 MPa, 50% MDI, 50% HDI-PPBG foam had a similar storage modulus of 0.46 MPa and the HDI foam had stiffness an order of magnitude higher at 3 MPa. T_g for these foam samples were determined from the peak of the tan δ curve. T_g for the foams can be seen in Table 2.6.

Table 1.6 T_g results for foams calculated from tandelta

Sample	T_g (°C)
MDI-PPBG	150
50% MDI, 50% HDI-PPBG	90.92
HDI-PPBG	55.46
Commercial memory foam	45.32

While testing it was noted that empirically the HDI-PPBG foam felt much like a memory foam. A memory foam is a type of shape memory polymer that can temporarily take one a new shape and recover the original shape after a period of time, heating, or some other applied stimuli.[40-43] This phenomenon is related to a foam being used in the temperature window that T_g occurs. The most common example a consumer may encounter on a regular basis is memory foam mattress products. An Allswell branded 3” Memory Foam Mattress Topper was purchased to compare to the HDI-PPBG foam. While the exact composition of this commercial foam is not known, it is known to be a polyurethane foam that had a strong amine odor upon removing from the package which dissipated after 24 hours. Figure 2.5 d) shows the DMA of the memory foam. Compared to the DMA of the HDI-PPBG foam in Figure 2.5 c), the behaviors of E’, E” and tan δ align well. The Allswell memory foam had two maxima in E’ at -20^{o}C and 22.26^{o}C, a T_g at 45.32^{o}C which are all comparable values to the HDI-PPBG foam. The only difference being the maximum G’. The maximum G’ for the commercial memory foam was 0.26 MPa, indicating a lower stiffness in the same magnitude of the MDI containing PPBG foams.

It is well documented that aromatic urethanes can discolor after UV or thermal aging from a variety of oxidation reactions on the urethane, thermal degradation is especially seen at temperatures at or above 160°C.[39] These reactions do not happen with aliphatic urethanes, such as those produced with HDI. Figure 2.6 shows the foam samples after one DMA cycle in which foams were subjected to a temperature sweep from -20-180°C. 100% MDI foams exhibited the most discoloration, while 100% HDI foams exhibited little to no degradation and the blended foams exhibiting discoloration in between. This is an especially important advantage to foam products in which consumers can see the foam and any discoloration can cause concern.

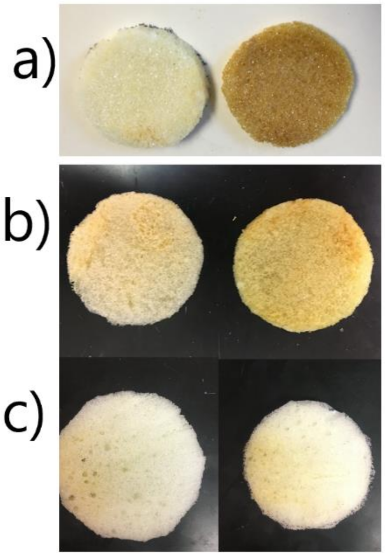

Figure 2.6 Foam samples after one cycle of DMA testing. a) is MDI-PPBG, b) is 50% MDI, 50% HDI-PPBG and c) is HDI-PPBG

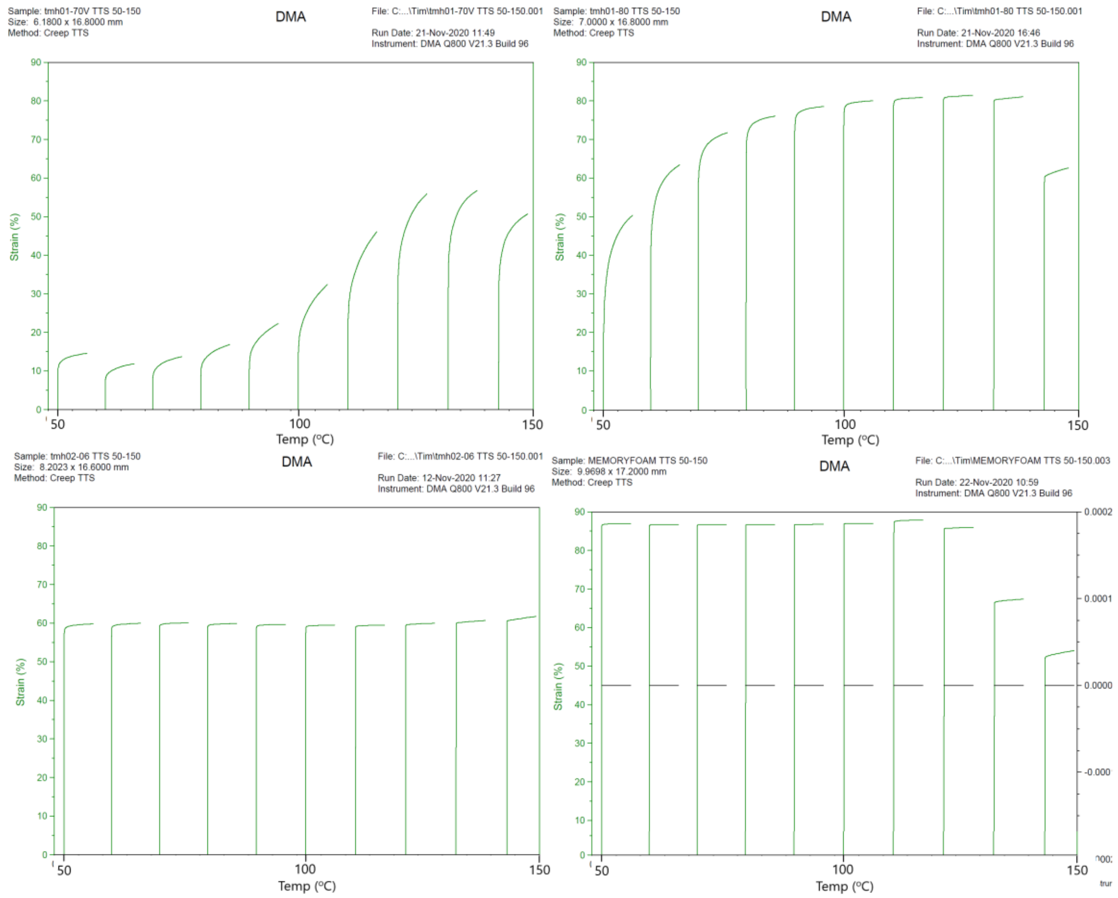

Figure 2.7 DMA creep results for a) MDI-PPBG foam, b) 50% MDI, 50% HDI-PPBG, c) HDI-PPBG and d) commercially available memory foam

Creep is the permanent deformation of a polymer after the application of persistent mechanical stress. DMA can study this behavior by applying a constant load and measuring the strain.[49-51] To explore this in the PPBG foams, a temperature sweep from 50^{o}-150^{o}C was run with a static force of 0.1N a displacement stress of 0.01 MPa, an temperature equilibrating time of 5 mins, displacement time of 15 mins, and a 10^{o}C temperature step between each step. Figure 2.7 shows the results from that study. Figure 2.7 a) shows the MDI-PPBG foam sees a rise in the stain against the static force starting at 90^{o}C indicating that the material is undergoing stiffening under the load which could be a result of the polymer becoming brittle from backbone degradation. 50% MDI, 50% HDI-PPBG, Figure 2.7 b), shows this increase in strain over time right at 50^{o}C before equalizing 90^{o}C before dropping off at 150^{o}C. This sudden softening of the material could be indicative of the foam yielding and cells collapsing. The HDI-PPBG foam has a consistent strain through the measured range (Figure 2.7 c). Figure 2.7 d shows the commercially available memory foam with a consistent strain over the temperature range until a drop of beginning at 140^{o}C. All of the foams but the HDI-PPBG foam degraded is supported by Figure 2.7, which shows that after creep testing, all foams underwent permanent deformation except for the foam based on 100% HDI. This further indicates that the HDI-PPBG foam is better able to withstand repeated sustained use for longer than the comparable MDI foams.

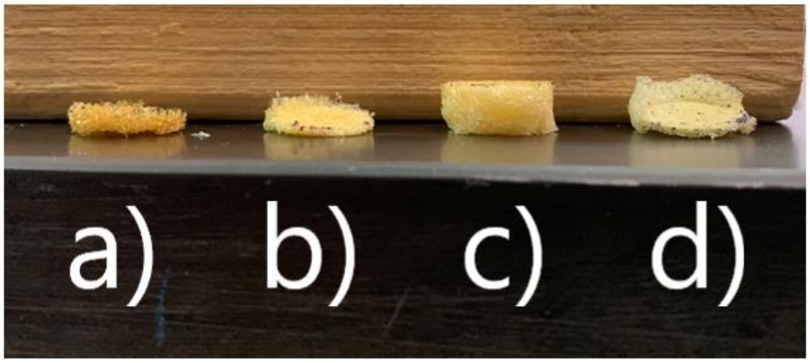

Figure 2.8 Foam samples 24 hrs after creep study from left to right a) MDI-PPBG, b) 50%MDI 50%HDI-PPBG, c) HDI-PPBG, and d) commercial memory foam

The HDI-PPBG foams produced for this study outperform the MDI-PPBG foams in several key areas. They are more resistant to discoloration and permanent deformation; they have a storage modulus an order of magnitude higher than the comparable MDI foams and commercial memory foams and show memory foam-like behavior. This is a great indication that a HDI-PPBG foam could be produced with industrially significant properties, such as a memory foam, and be able to be industrially composted after the end of life of the product.

4. Conclusion

HDI-PPBG based foams outperformed similar foams based on TDI-PPBG and PMDI-PPBG in respirometry tests for industrial composting yielding 64% absolute biodegradation after 180 days at 50°C. The TDI-PPBG and PMDI-PPBG foams showed negligible biodegradation at -5.3% and 8.05%, respectively. Cohesive foams were synthesized with the slower reacting aliphatic HDI by producing PPBG prepolymers end capped with HDI and otherwise using the standard two shot method of polyurethane foam production. The HDI-PPBG foams produced exhibited memory foam-like behavior similar to commercially available memory foam mattresses. Moreover HDI-PPBG foams showed greater resistance to discoloration due to heat and better resistance to permanent deformation after DMA testing than similar PMDI-PPBG foams. HDI-PPBG foams show a great potential as a memory foam product that contains 32wt% bio-based PPBG polyols and has the potential to be industrially compostable.

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CHAPTER 3

PREPARATION AND BIODEGRADATION OF ISOCYANATE BASED ADHESIVE FOR MULTILAYER FILMS[1]

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[1] Henkel, T. and Locklin, J. To be submitted to ACS Sustainable Chemistry & Engineering.

Abstract

This work probes the biodegradation of multilayered films comprising of polyhydroxyalkanoate (PHA) and metallized viscose adhered with a bio-based polyurethane prepolymer synthesized from poly(1,3-propylene-1,4-butylene glutarate) (PPBG) and sebacic acid diisocyanate (SADI). It was found that these films could be made catalyst-free and in a home composting study, exhibited after 117 days 42.56% at 20^{o}C degradation and 85.96% degradation at 35^{o}C.

Introduction

The vast majority of consumer goods available today involve packaging film. As of 2012 the market in the United States alone consisted of 13.6 billion pounds of volume with 88.5% of that consisting of polyethylene and polypropylene based films.[1] Polyethylene and polypropylene have a myriad of excellent properties from strength, flexibility, moisture barrier, to inertness.[2-3] One large drawback from these polymers, especially in the case for temporary use packaging, is their resistance to biodegradation without the use of exotic enzymes and conditions.[4-5] Packaging films in industry are generally comprised of multiple layers with each layer fulfilling a different need. For example, a typical film could comprise of three layers: viscose, polyethylene, and an acrylic adhesive. The viscose provides an easily printable layer but has very low strength and flexibility which is overcome by the polyethylene layer which reenforces the viscose while the acrylic adhesive binds the layers together. In this way manufacturers can produce films with the desired properties for the application.[1]

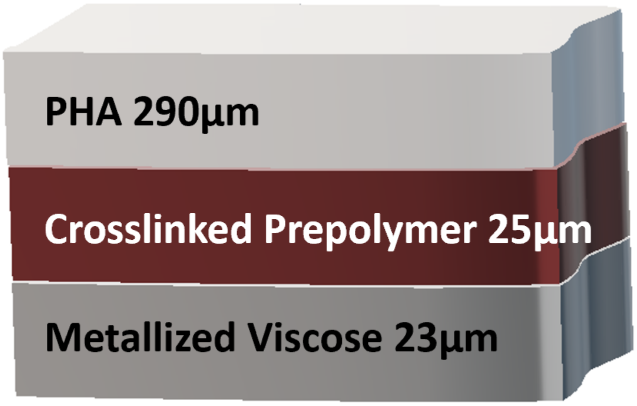

Figure 3.1 Representation of multilayered film

As multilayered packaging serves a temporary role in protecting a product before being ultimately discarded, much work has been done on trying to produce films that will biodegrade after use.[6-9] Due to their high reactivity and ability to react with hydroxyls, amines, carboxylic acids and water, isocyanates and isocyanate prepolymers are widely used as adhesives. The simplest forms are cured with ambient moisture in the air. After an isocyanate adhesive is applied, isocyanates will readily polymerize with atmospheric water forming polyureas. Any branch points in prepolymers give physical crosslinking points while the polymer chain length allow for chain entanglement giving rise to a strong adhesive. [10,13-18]

In this work a multilayered film is produced from metallized viscose, polyhydroxyalkanoate (PHA) adhered together with a isocyanate prepolymer synthesized from poly(1,3-propylene-1,4-butylene glutarate) (PPBG) and sebacic acid diisocyanate (SADI). These films were evaluated for biodegradation in home composting using respirometry at 20°C and 35°C.

Experimental Section

Materials

Glutaric acid was purchased from Sigma Aldrich. 1,4-butanediol (BDO) and 1,3-propanediol (PDO) were purchased from Sigma Aldrich. 1,4-Diazabicyclo[2.2.2]octane 2-(DABCO) was purchased from Sigma Aldrich. Bismuth 2-ethylhexanoate was purchased from Alfa Aesar. Dow Corning® 5987 Additive High-efficiency surfactant was provided via sample from Dow Corning®. Triethanol amine was purchased from Sigma Aldrich. Hexamethylene diisocyanate (HDI) was purchased from Acros Organics.

Methylenediphenyl-4,4'-diisocyanate (MDI), mixture of di and triisocyanates, was purchased from MilliporeSigma. Glycerol and pentaerythritol was purchased from Sigma Aldrich.

Synthesis of Poly(1,3-propylene-1,4-butylene glutarate) (PPBG)

All PPBG polymers were synthesized via condensation polymerization. Glutaric Acid, BDO and PDO were placed in a 3-neck round bottom flask with stir bar, dean stark and condenser. Reaction was conducted at atmospheric pressure and 165-175^{o}C removing condensed water for 2 hours, if a branched polymer was desired glycerol or pentaerythritol were added and vacuum pulled for up to 48 hours, depending on desired molecular weight. Linear PPBG with a molecular weight of 3648 g/mol was produced at a 500g batch size at 175^{o}C over 41 hours with a molar ration of 0.5mol% glutaric acid, 0.25mol% BDO, and 0.25mol% PDO. A branched PPBG with an average functionality of 3.7 and molecular weight of 8864 g/mol was produced at a 300g batch size at 175^{o}C over 43 hours with a molar ration of 0.5mol% glutaric acid, 0.23mol% BDO, 0.23mol% PDO and 0.02mol% glycerol.

Synthesis of Isocyanate Prepolymers

A molar ratio of reactive groups, -NCO:-OH, of 2:1.05 was used for the isocyanate and PPBG feed ratios. Sebacic acid diisocyanate (SADI) was diluted to 30% by weight in dry acetone, placed in a round bottom flask under N_2 atmosphere and heated to 60^{o}C. PPBG was diluted to 50% with dry acetone and fed in at ~0.2 mL/min. After full addition of PPBG, reaction was allowed to proceed for additional 12-48 hours. Product was then dried via vacuum distillation.

Preparation of Multilayered System

A Carver Model 4386 Bench Top Laboratory Manual Press with Electrically Heated 6” Platens was used to form multilayered systems. Metallized viscose, 23µm thickness, was supplied by (NatureWorks). Polyhydroxyalkanoate (PHA) polymer films were pressed to 290 µm thickness on the Carver press using 10,000 lbs pressure at 60°C for 15 seconds. Isocyanate prepolymer blends at a weight ratio for linear prepolymer to branched prepolymer of 4:1 were prepared as the binder for the layers. 0.6g of isocyanate prepolymer blends were weighed onto 15.24 cm x 15.24 cm square of metallized viscose (metallized side up) and a 15.24 cm x 15.24 cm square of PHA film was placed on top of the prepolymer. A typical weight for the full multilayered film was 9.8 g with 8.4 g comprising the PHA, 0.8 g comprising the viscose and 0.6 g comprising the adhesive. Release paper was placed on both sides of the sample and placed in the Carver press 5,000 lbs pressure at 75°C for 30 seconds, then held at 75°C with ~10lbs pressure for 15 minutes. Samples were then removed and allowed to cure at 50°C in an oven overnight.

Characterization of Polymers

Molecular Weight

Molecular weight of PPBG polymers were determined by gel permeation chromatography (GPC). The GPC system consisted of two Shimadzu, LC-20AD pumps, a Shimadzu, SIL-20A automatic sampler, a Shimadzu, CTO-20A column oven, a Shimadzu, SPD-20 A ultraviolet detector, and a Shimadzu RID-10A refractive index detector. The system used chloroform as the mobile phase at a flow rate of 1.0 mL/min, and the molecular weight is reported relative to polystyrene standards.

Hydoxyl Number[10]

Hydroxyl number (OH#) is a measure of the concentration of hydroxyl end groups in a polymer. It was calculated using the following equation.

$$OH\# = \frac{56100 * Polymer\ functionality}{Molecular\ Weight}$$

With the molecular weight being determined by GPC and functionality calculated from monomer feed ratios of the PPBG polymers.

Respirometry

An ECHO respirometer (Slovenske Konjice, Slovenia) was used in this test. 200 mL/min air flow was pumped into each reactor and the composition of exhausted gas was analyzed by the built-in gas sensors. The raw compost used was collected from a 4-5 month old batch from an industrial composting plant located in Athens, Georgia. Forest residue, food waste and livestock manure were generally used as feedstock in this composting plant. Temperature in the composting pile (30 cm depth) was 50^{o}C at the collecting time. The raw compost was sieved using 4.76 mm sieve to make the fine compost inoculum. The Reactor assay consisted of:

- Blank: 250 grams of compost inoculum only, triplicate
- Cellulose (positive control): 250 grams of compost inoculum and 6 grams of cellulose in triplicate

- Polyethylene (PE) (negative control): 250 grams of compost inoculum and 6 gram PE in triplicate
- Sample 1 to 9: 250 grams of compost inoculum and 6 grams of sample in triplicate at 2 temperatures

The respirometer was operated for 117 days. During the operation, the mixture of compost and samples in each reactor was stirred once a week to avoid channeling and control compost moisture. The compost in each reactor was collected for the moisture test right after the stirring. Certain amount of DI water was added in the compost when the compost appeared to be dry. The amount of water used in the rehydration has varied depending on the sample.

The total solid, volatile solid, C%, N%, and pH of compost inoculum were analyzed. C% and N% of polymers were analyzed. pH was measured using the method described in ASTM 5338-15. Carbon and Nitrogen content were measured using the method described by Kirsten (1979)[11]. The compost moisture in each reactor during the test was measured by drying 0.2-2.0 g sample in 58°C oven to constant weight (weight change <5%).

Biodegradation numbers were produced by monitoring gas flow rate, gas moisture, gas pressure, gas temperature and CO_2 concentration in the gas to calculate the CO_2 evolution (gram) from each reactor. The biodegradation of each sample was calculated by subtracting the average blank compost inoculum CO_2 evolution from the CO_2 evolution of the samples and then being divided by ideal CO_2 evolution from each sample. All samples in triplicate were averaged together.

Results and Discussion

1. Isocyanate Choice and Formulation

Isocyanate based adhesives have been used extensively in industry and are widely available commercially. Prepolymers previously in Chapter 2 of this work made for incorporation in foams have similar structure to moisture cured adhesives used in industry. These prepolymers were explored to be used as adhesives to bind metallized cellulose to PHA. Isocyanates are toxic to both humans and microbiomes in compost and the prepolymers generated for the foam formulation work generally had >80 mol% free isocyanate, a level much too high to be used as a component in multilayered packaging. As of August 2020 the European Parliament and of the Council concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) amended Annex XVII to Regulation (EC) No 1907/2006 limiting the level of free diisocyanate monomers in consumer goods to <0.1wt%.[12] In order to reduce the potential for free isocyanates to cause harm and cause regulatory issues if commercialized, isocyanate prepolymers were formulated with excess polyol to ensure no free isocyanate monomers remained in the adhesives. Any free isocyanate monomer could be volatilized at elevated temperatures during production, application, or end use and can cause significant health problems and require mitigation efforts. In addition, even though after application any residual isocyanate will eventually react with atmospheric moisture and form urea, having free isocyanate monomer in the formulation can cause regulatory issues if used for packaging. Sebacic Acid Diisocyanate (SADI) was selected as the diisocyanate for this study. SADI is a linear, aliphatic diisocyanate.

Poly(1,3-propylene-1,4-butylene glutarate) (PPBG), PPBG, used for this study was a blend of a linear polymer with a molecular weight of 3648 g/mol and a branched polymer with a functionality of 3.7 and a molecular weight of 8864 g/mol. The linear prepolymer was chosen to aid in the flowability of the adhesive and contribute towards chain entanglement while the lightly branched prepolymer was added to provide some crosslinking as well as contribute to entanglement of the cured adhesive. PPBG was shown in Chapter 2.1 of this work to be able to be synthesized from renewable feedstocks.

It was observed in a laboratory setting that a stoichiometric ratio of 2:1 isocyanate end group (-NCO):alcohol end group (-OH) still yielded a prepolymer with an acrid isocyanate odor. The ratio was adjusted to 2:1.05 NCO:OH and no odor was detected. Higher ratios OH groups resulted in full polymerization and gelation of the reaction. IR confirmed the presence of unreacted isocyanate groups at 2260 cm^{-1} (Figure jdkj, 0 min). This initial study was to assess feasibility and potential for biodegradation of the viscose, prepolymer and PHA multilayered system, as such catalysts and crosslinking agents were omitted from formulations.

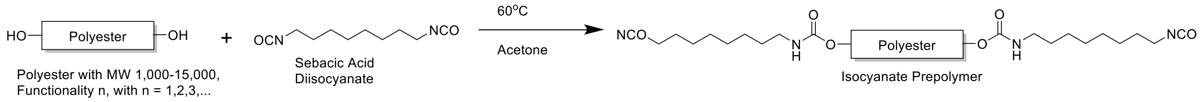

Figure 3.2 Synthesis of isocyanate prepolymer

2. Curing Conditions

To determine what curing conditions would be necessary for the catalyst-free ambient moisture curing of the SADI-PPBG, a PPBG diol with a molecular weight of

3648 g/mol film was coated onto metallized viscose and the disappearance of the isocyanate peak was observed via FTIR. The prepolymer was prepared by heating to 50°C to decrease viscosity and applied to metallized viscose with a 25.4 μm drawdown rod and placed in an oven at 60°C and ambient humidity. Portions of the sample were taken at various time intervals and an IR spectrum was taken (Figure 3.3). The presence of the peak at ~2270 cm^{-1} is indicative of the isocyanate functional group. This peak is present in prepolymer in IR spectra taken up to 60 minutes (Figure 3.3 0-60min). The film was able to be fully cured as indicated by the disappearance of the isocyanate peak at ~2270 cm^{-1} after curing overnight (Figure 3.3 1080 minutes). This was further reinforced by the film being tack free after curing overnight.

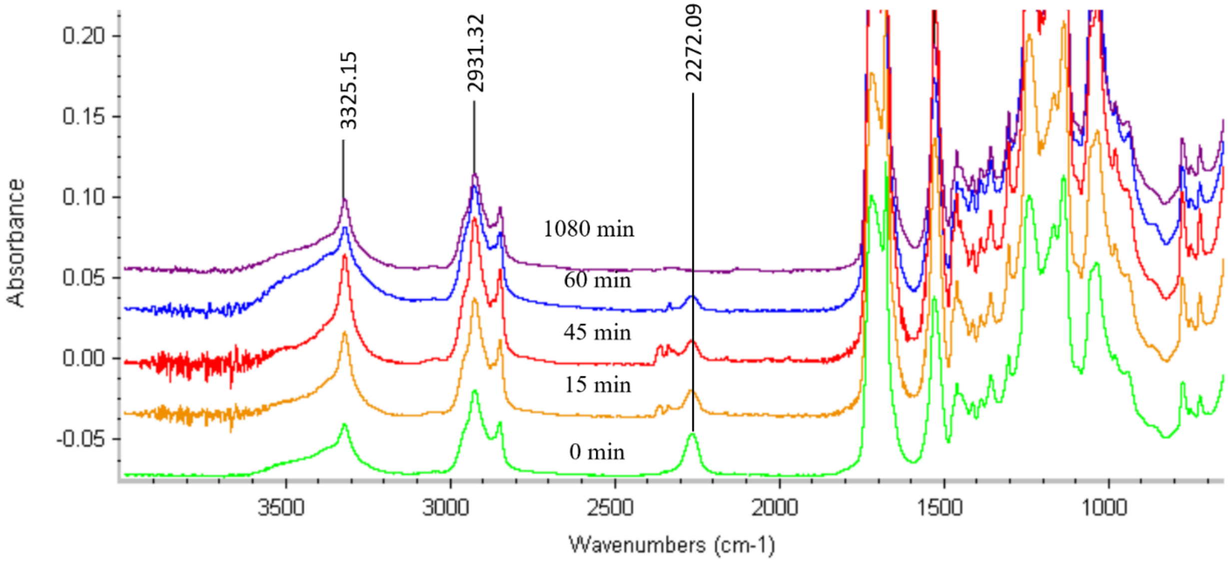

Figure 3.3 IR of isocyanate prepolymer curing catalyst free at 60°C, ambient humidity.

Multilayered samples were prepared using a blend of the two isocyanate prepolymers with metallized viscose and PHA outlined in the methods section. Initial samples were attempted with linear SADI-PPBG alone, but the resulting films showed no adhesion after curing and simply fell apart. A branched SADI-PPBG was introduced to the linear prepolymer to allow for some crosslinking to improve polymer entanglement and increase adhesion. A ratio of 4:1 linear to branched by weight was selected as it improved adhesion of the films while still being wettable and forming a uniform adhesive layer. After preparing the samples, the PHA and viscose layers were then peeled apart by hand immediately and after curing overnight at 60^{o}C. Figure 3.4 shows the films peeled

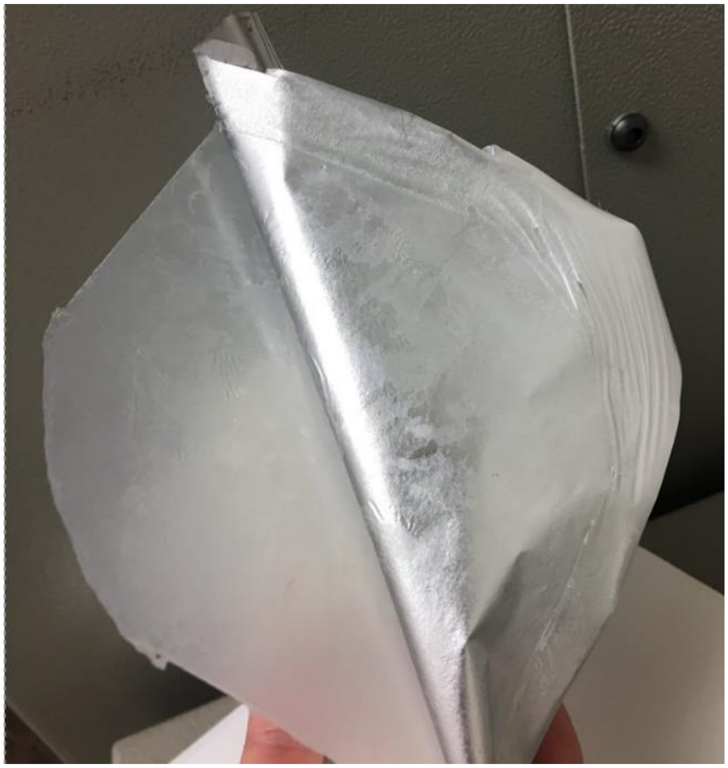

Figure 3.4 PHA (left) adhered to metallized viscose (right). Adhesive can be seen on both layers after peeling apart.

apart after curing. Adhesive remnant can be seen on both the PHA and viscose indicating both adhesive and cohesive failure. IR spectra was taken on areas of the films where there was cohesive failure and polymer still attached to ascertain if the adhesive was fully cured and no presence of the isocyanate peak at ~2270 cm^{-1}. Figure 3.5 a) shows the isocyanate's asymmetric stretch at 2272.18 cm^{-1} in the uncured adhesive after being peeled apart and is absent in the sample that was cured overnight (Figure 3.5 b) indicating that these multilayered films can be cured catalyst free at 60°C over 18 hours.

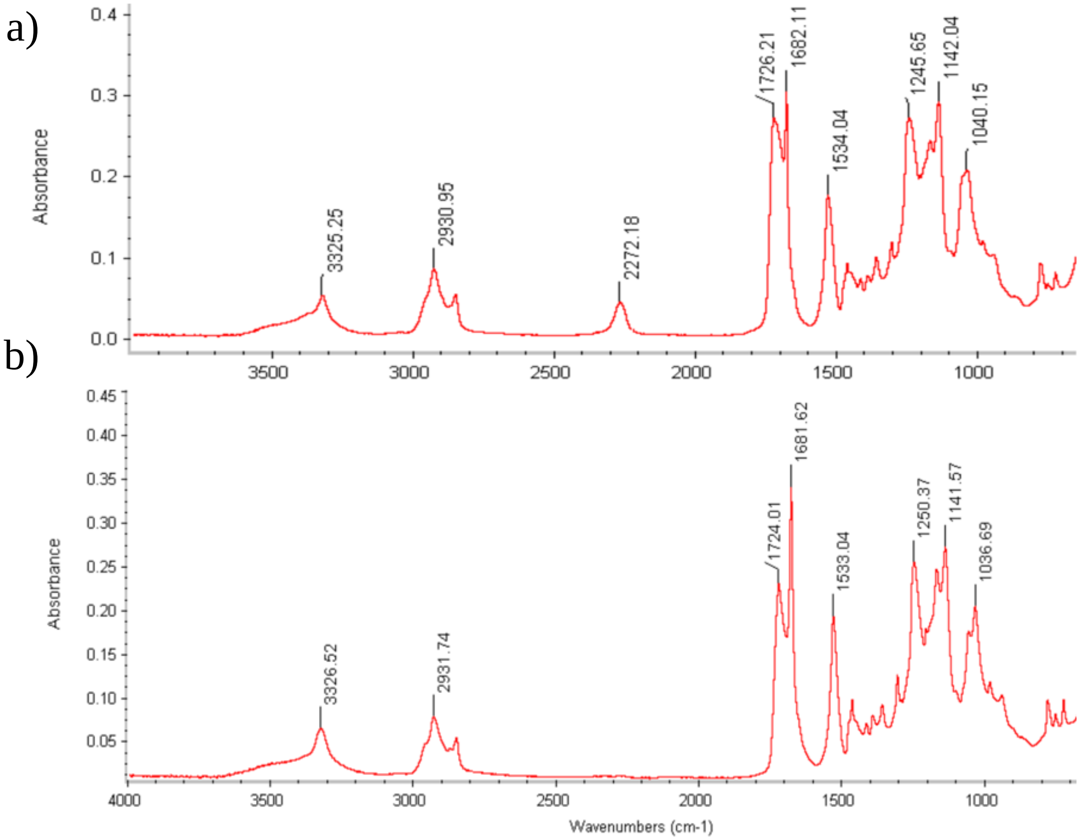

Figure 3.5 a). Uncured isocyanate prepolymer in multilayered system before curing **b).** prepolymer after curing at 60°C overnight.

3. Biodegradation of Films

Multilayer films were then prepared for respirometry at 20^{o}C and 35^{o}C to replicate conditions found in a typical home compost. These conditions are less harsh than industrial composting conditions where temperatures can reach $50\text{-}60^{o}$C and are more representative of the effective conditions where a majority of multilayered packaging will end up after use. The viscose films alone and the PHA films alone were also compared. Polyethylene (PE), one of the most pervasive plastics commonly used for packaging, was added as a negative control while cellulose was added as a positive control.

Figure 3.6 shows the absolute biodegradation of the films at 20^{0}C and 35^{o}C over 117 days and Table 3.1 shows the final numbers. As expected, polyethylene shows little to no bioactivity over the 117 day time scale at either 20^{0}C or 35^{o}C. At 20^{o}C PHA essentially matches cellulose's biodegradation rate and ends slightly lower (24.27% for PHA vs 24.7% for cellulose). Viscose, and the multilayer film both exceed cellulose's biodegradation at 72.65% and 42.56% respectively. The multilayered film results agree with the wt%. contributions of each component individually. By multiplying the wt% contributions of 70 wt% for PHA and 25 wt% for viscose with their individual biodegradation results and summing the values together the result is 26.9%, which is in significantly lower than the observed rate of 42.56% for the multilayered film indicating there is some synergistic effects occurring in the multilayered films causing them to outperform the individual films themselves. This warrants further investigation as to what is causing the beneficial interactions.

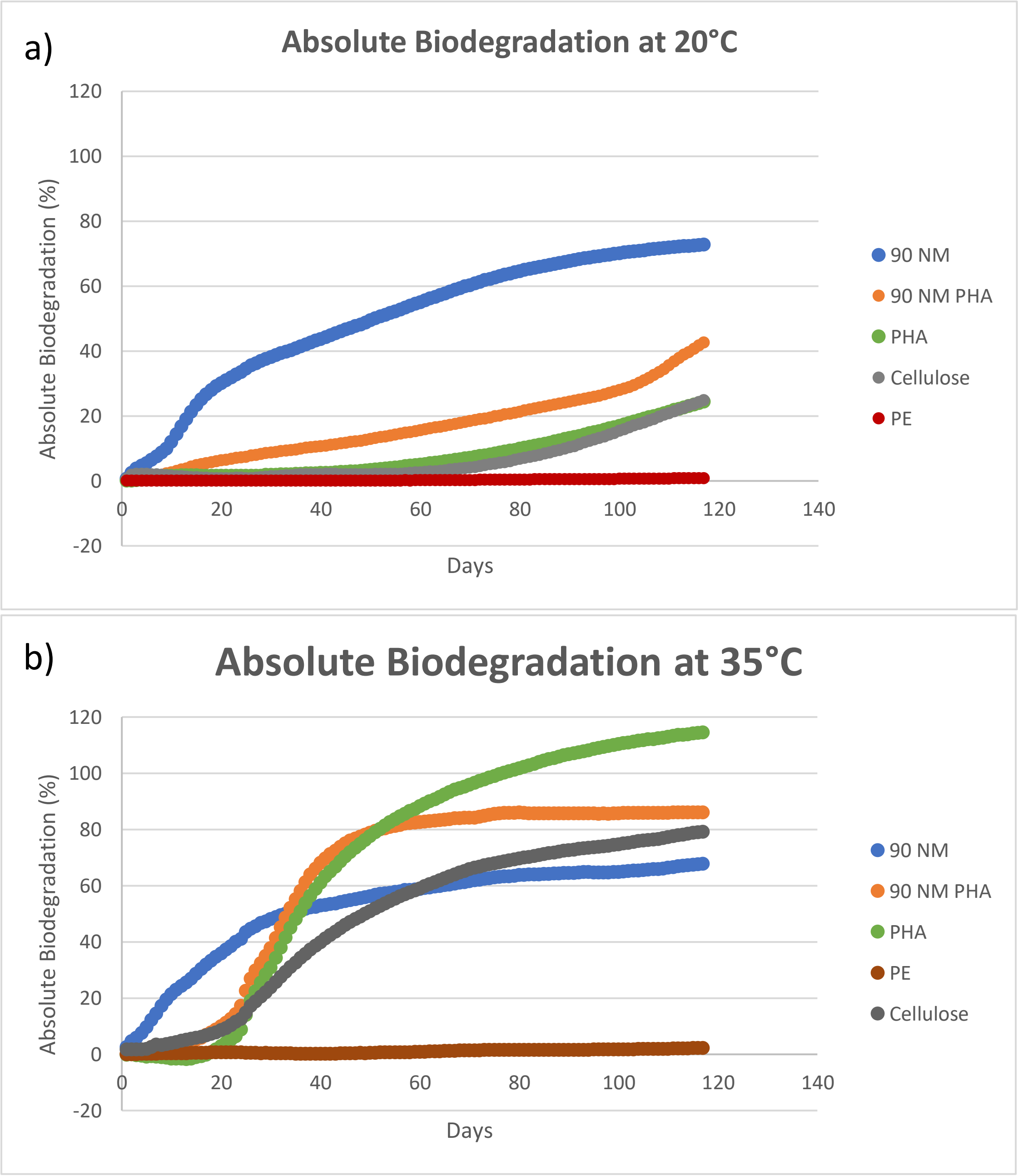

Figure 3.6 Absolute Biodegradation results for films after 117 days at a) 20^{o}C and b) 35^{o}C

Table 3.1 Final absolute biodegradation values for 117 days

Sample	20°C Biodegradation (%)	35°C Biodegradation (%)
Metalized Viscose	72.65	67.74
Viscose-SADIPPBG-UGA PHA	42.56	85.96
UGA PHA	24.27	114.44
Cellulose	24.70	79.14
PE	0.71	2.18

At the higher temperature of 35°C the compost is more active, and all of the films exhibit higher biodegradation results with the exception of the viscose film which exhibits a decrease of 4.91% to 67.74%. While the multilayered film shows a higher biodegradation of 85.96% at the elevated temperature, the PHA film exceeds this by achieving 100% biodegradation by 80 days while the multilayer film's biodegradation rate appears to be plateauing at this point. By comparing the individual contributions by wt% as done at 20°C the value at 35°C the expected biodegradation is 103.4% degradation, which is higher than the 85.96% degradation observed. While not ideal, this is still a high degree of biodegradation in home composting.

Table 3.2 Wt% of multilayer film components

Film Layer	Wt.%
PHA	85
Viscose	9
SADI-PPBG Prepolymer	6

4. Conclusion

PHA and viscose were able to be glued together using a PPBG-SADI isocyanate prepolymer adhesive forming a multilayered film. The PPBG-SADI prepolymer can be synthesized from bio-based monomers, catalyst free. After 117 days at both 20^{o}C and 35^{o}C the multilayer films show biodegradation results in a home composting scenario of 42.56% and 85.96%. These are promising results that indicate multilayered films comprising of a PPBG-SADI isocyanate adhesive could be a compostable, bio-based option for industrial produced multilayered films. Further work is necessary on properties such as increasing adhesion, evaluating film strength, printability, and moisture barrier to fully evaluate whether this technology is a commercially viable option.

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CHAPTER 4

CONCLUSIONS AND FUTURE OUTLOOK

Conclusions

This work focused on producing biodegradable polyurethane systems with a focus on using bio-based feedstocks when possible. By copolymerizing PPBG, a polyester that can be made from bio-based monomers, with HDI and SADI, polyurethane systems were created that had the ability to biodegrade. Foams synthesized utilizing PPBG-HDI prepolymers were able to be formulated using a conventional two shot method producing water blown foams that high likely-hood of biodegrading and were 37% bio-based and 64% absolute biodegradation after 180 days under industrial composting conditions. The PPBG-HDI foams synthesized exhibited memory foam-like behavior under DMA testing that was comparable to commercially available memory foam mattresses. The PPBG-HDI foams showed a greater resilience to deformation under high temperature testing versus the PPBG-MDI foams and the commercially available product. Multilayered films consisting of PHA adhered together with viscose using PPBG-SADI exhibited biodegradation of 42.56% at 20^{o}C and 85.96% at 35^{o}C under home composting conditions.

Future Work

PPBG has great potential to be a bio-based polyol in polyurethane systems that, when reacted with the linear aliphatic isocyanates HDI and SADI, can lead to a material that is biodegradable in industrial and composting environments. PPBG can be made in batch mode type reactors and should have no issues being produced on and industrial scale.

The next step for the PPBG-HDI based foams should be to scale up formulations and see if making a large-scale slab-stick type foam is possible with current iterations. The current iteration could be industrially relevant in a memory-foam type application, more rigorous testing of material properties with industrial benchmarks to meet should be further explored.

Further work is required to optimize PPBG-SADI prepolymers as adhesives. While the prepolymers were able to adhere PHA films to viscose, they were easily peeled apart by hand. A study varying the size and branching of the PPBG in conjunction with peel tests to accurately measure the amount of force required to delaminate films should be able to optimize the adhesive strength of PPBG-SADI. Once the adhesive has been optimized, films need to be tested against industry standards for films such as moisture-barrier tests.

APPENDIX A

NMR SPECTRA OF COMPOUNDS

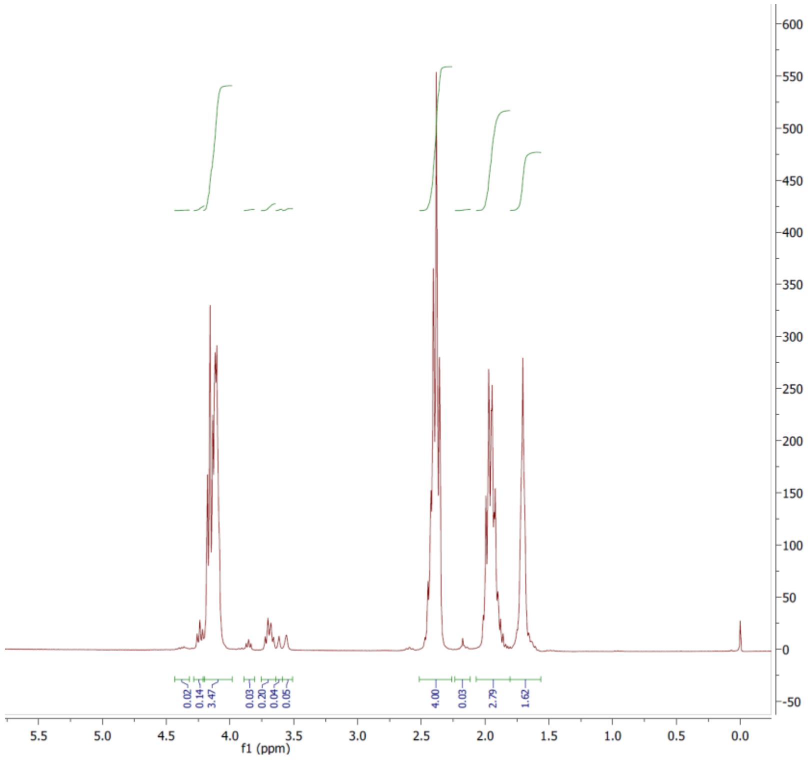

Figure A1 ^{1}H NMR of Branched Glutarate

Table A1 Molar feed ratios of branched glutarate

Glutaric Acid	0.5
Butanediol	0.23
Propanediol	0.23
Pentaerythritol	0.04

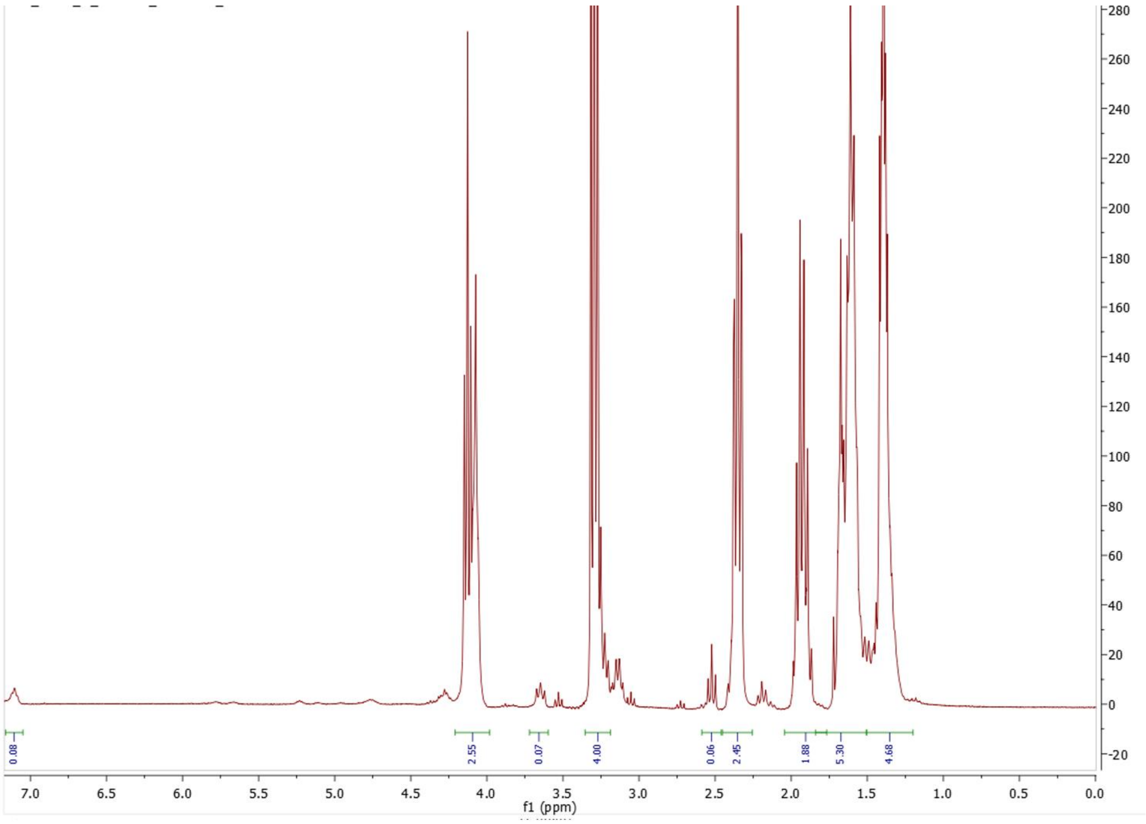

Figure A2 ^{1}H NMR of PPBG-HDI prepolymer

Table A2 Feed ratios for PPBG used for PPBG-HDI prepolymer, final %NCO: 30.4%

Monomer	Mol%
Glutaric Acid	0.5
Butanediol	0.23
Propanediol	0.23
Glycerol	0.02

APPENDIX B

GPC SPECTRA OF COMPOUNDS

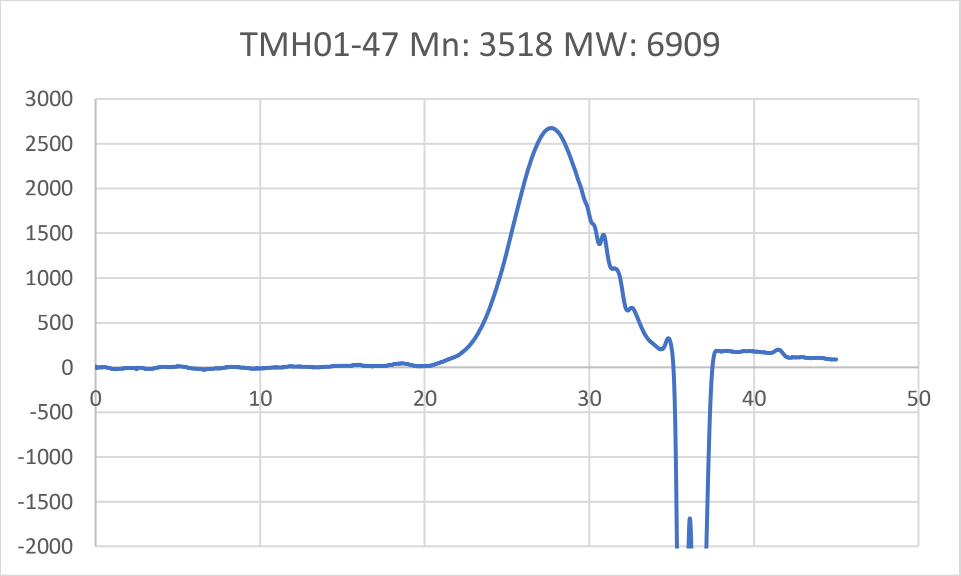

Figure B1 GPC of PPBG MW 6909 g/mol

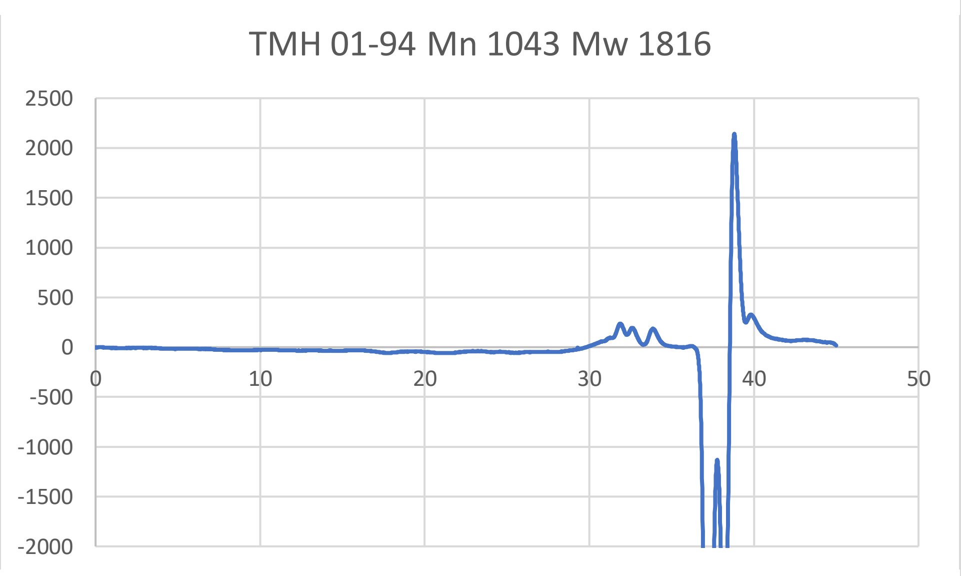

Figure B2 GPC of PPBG MW 1816 g/mol

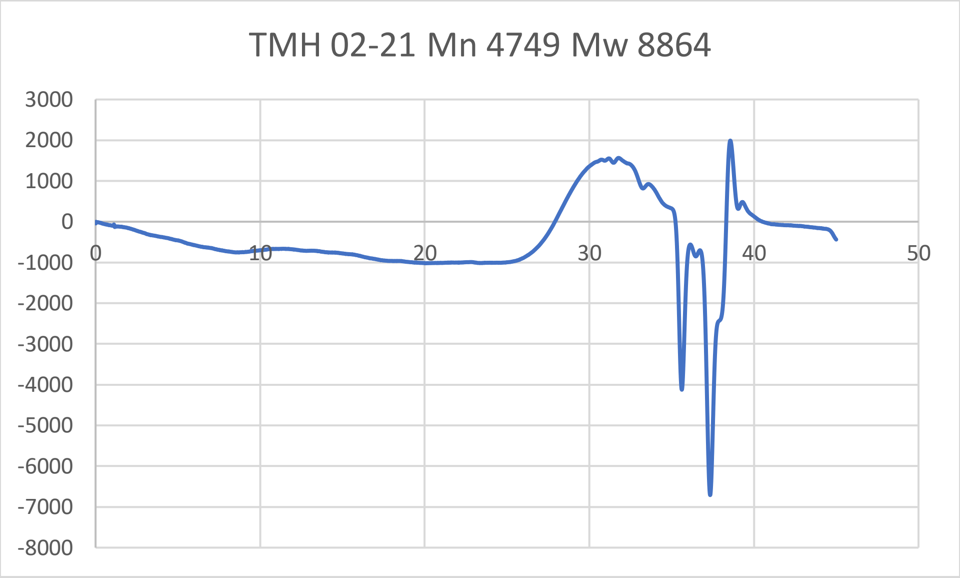

Figure B3 GPC of PPBG MW 8864 g/mol

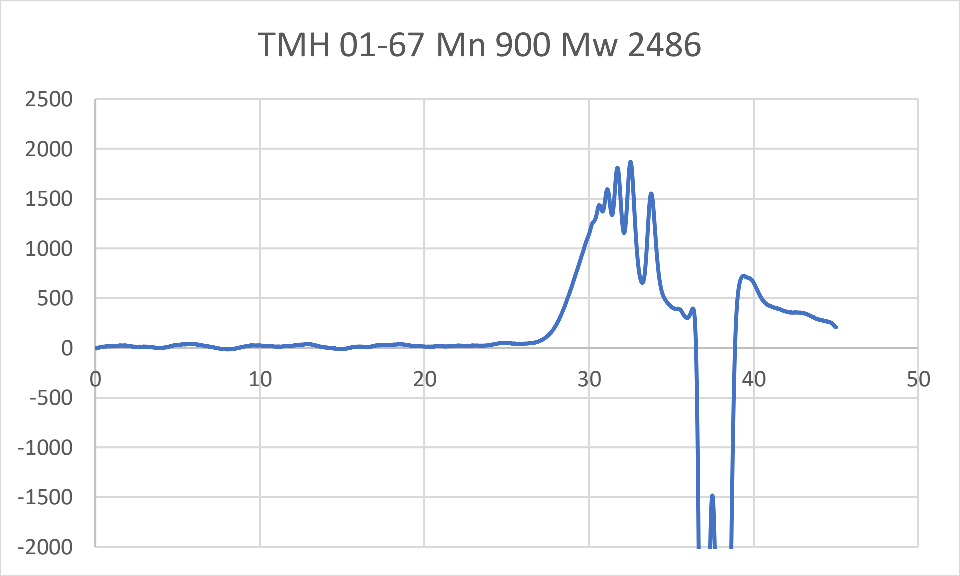

Figure B4 GPC of PPBG MW 2486 g/mol

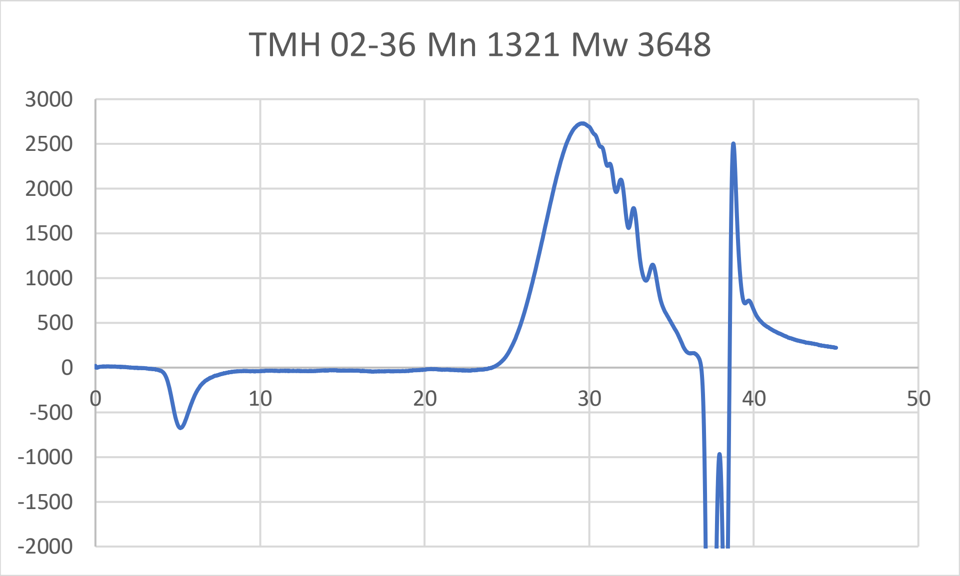

Figure B5 GPC of PPBG MW 3648 g/mol