# SYNTHESIS AND CHARACTERIZATION OF BIO-BASED POLYURETHANES

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# ABSTRACT

Hybrid polyurethanes are commonly made by reacting two chemical building blocks: a polyol and diisocyanate, followed by end-capping with appropriately functionalized silanes to permit moisture curing. This project aims to provide a framework to fully characterize an industrial sealant resin, before incorporating bio-based polyols and isocyanates into the original formulation. The original formulation is derived from petroleum-based monomers. By substituting bio-based molecules in the place of both building blocks, the resulting commercial product will have a higher renewable content. In recent years, finding bio-based alternatives for petroleum products has become a focus of research and industrial efforts in order to decrease petroleum consumption. The industrial partner's (Adfast Corp.) original product was replicated on a small scale and benchmarks for the molecular weight, viscosity, and stress-strain properties were determined. Gel permeation chromatography (GPC) was used to evaluate and compare the molecular weight distributions of multiple resins. Knowing the molecular weight distribution permitted the elucidation of the relationship between the molar ratio of diisocyanate to polyol in terms of chain length (dimer, trimer formation etc.). Once the original resin was fully characterized, three different bio-based polyols were selected and substituted in place of the original petroleum-based polyol. These new formulations were tested in the same manner as the original formulation, and the molecular weight distributions, viscosities, and stress-strain properties were compared. Of the three polyurethanes produced using bio-based polyols, one, using the commercial Myrinol™ DG-110 polyester polyol, showed promising physical properties: having high elasticity and tensile strength. This formula was then further optimized by the incorporation of a bio-based isocyanate: L-lysine diisocyanate. The properties of this final resin were measured and compared to the original petroleum-based product. It was found that by incorporating the bio-based isocyanate, the physical properties of the PU became more similar to Adfast's original resin. With additional testing (scale-up, adhesion testing, UV stability etc.) and optimization there is potential to have partial and fully bio-based polyurethanes incorporated into Adfast's product line. This project has opened doors for Adfast and McGill to pursue different avenues in order to develop a competitive, commercial bio-sourced product.

# RÉSUMÉ

Les polyuréthanes hybrides sont généralement fabriqués en faisant réagir deux monomères, un polyol et un diisocyanate, puis en les modifiant avec des silanes fonctionnalisés de manière appropriée pour permettre la réticulation au contact de l'humidité. Ce projet vise à caractériser complètement une résine d'étanchéité industrielle, avant d'incorporer des polyols et des isocyanates biosourcés à la formulation d'origine. La formulation originale est obtenue à partir de monomères à base de pétrole. En substituant ces deux composants par des monomères biosourcés, le produit commercial obtenu aura un fort contenu renouvelable. Au cours des dernières années, la recherche de solutions à base de produits biosourcés pour remplacer les produits pétroliers est devenue primordiale. Le produit original du partenaire industriel (Adfast Corp.) a été répliqué à petite échelle et des critères de référence comme la masse molaire moyenne, la viscosité, et la résistance à la traction ont été déterminés. La chromatographie par perméation de gel (GPC) a été utilisée pour évaluer et comparer les distributions de masses molaire moyennes de la résine. Connaître la distribution de la masse molaire moyenne a permis d'élucider la relation entre le rapport molaire diisocyanate/polyol et la longueur de chaîne moyenne (dimères, formation de trimères, …) Une fois que la résine industrielle fut entièrement caractérisée, trois différents polyols biosourcés ont été sélectionnés afin de substituer le polyol provenant de ressources pétrolières. Ces nouvelles formulations ont été testées de la même manière que la formulation d'origine et la distribution de la masse molaire moyenne, la viscosité et les propriétés en contrainte-déformation ont été comparées. Parmi les trois polyuréthanes produits à partir de polyols biosourcés, celui à base de polyol Myrinol™ DG-110 a présenté des propriétés physiques prometteuses. Cette formule a ensuite été optimisée par l'incorporation d'un isocyanate d'origine naturelle: le diisocyanate de L-lysine. Les propriétés de cette résine finale ont été mesurées et comparées au produit original à base de pétrole. Avec des tests supplémentaires (échelle industrielle, tests d'adhérence, stabilité UV, ...) et une optimisation, il est possible d'inclure un polyuréthane entièrement biosourcé dans la gamme de produits d'Adfast.

# ACKNOWLEGMENTS

I would first like to thank my supervisor Dr. Milan Maric for giving me the opportunity to come to McGill and pursue graduate studies, as well as for his guidance and support throughout my master's.

Thank you to the rest of the Maric group for their help in the lab, their friendship, and for their passion for having cake at all group meetings. You all made McGill feel like home and made my time here so memorable. Special thanks to Adrien, Sharmaine, Faezeh, Saeid, Georges, and Roya for training me to use lab equipment and helping me to troubleshoot my experiments.

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Last but not least: thank you to my parents, Susan and Shane, for their constant love and support (emotional, financial and academic) throughout my undergraduate and master's degrees. You both are examples of the kind of engineer, mentor, and person I aspire to be. Thank you for instilling in me the desire to always do my best and for loving me unconditionally while I try to do so. Here's to me being financially independent now!

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| Đ | dispersity |
| FTIR | Fourier-transform infrared spectroscopy |
| GPC | gel permeation chromatography |
| IPDI | isophorone diisocyanate |
| LDI | ethyl ester L-lysine diisocyanate |
| MSDS | material safety and data sheet |
| $M_n$ | number average molecular weight |
| $M_p$ | molecular weight of highest peak |
| NIPU(s) | non-isocyanate polyurethane(s) |
| $^1$H-NMR | proton nuclear magnetic resonance spectroscopy |
| P(MMA) | poly(methyl methacrylate) |
| PPG | poly(propylene glycol) |
| PU(s) | polyurethane(s) |
| THF | tetrahydrofuran |

# CONTRIBUTION OF AUTHORS

The following manuscript is primarily the work of the author with contributions by Dr. Adrien Métafiot, Adfast's technical team, and Dr. Milan Maric.

Dr. Adrien Métafiot performed the $^{1}$H-NMR analysis to determine the structures of the bio-based polyols in Section 4.3.

Adfast's technical team: Sergio Andres Perez, Sergio Murillo, and Yves Dandurand, kindly provided a majority of the raw materials used, in addition to their technical guidance throughout the entire project. They also performed the analysis to determine the water content of the bio-based polyols in Section 4.3.

Dr. Milan Maric supported the experimental planning and helped in editing the manuscript.

## 1.0 INTRODUCTION

Due to the decline in the world's petroleum resources, advances in renewable petroleum substitutes have become a large focus of academic and industrial research.[1] Of the global annual oil production, ~8% is used in the production of polymers.[2] Of this 8%, half is converted directly from petrochemicals into polymer products. The energy demands of polymer manufacturing processes account for the remaining 4%.[3] From both an environmental and social perspective, bio-based polymers have developed a significant demand.[4] Compared to the 330 million tons of worldwide plastic production in 2016, 2 million tons of bioplastics were produced in 2017.[5] The global market for bioplastics is predicted to grow 20% per year between 2017 and 2022.[5] Polyurethanes, traditionally formed by reacting hydrocarbon derived polyols and isocyanates, are one area which has gained much attention recently. Polyurethanes are used to manufacture a wide range of foams—for furniture, packing, and insulation—as well as adhesives, sealants, and coatings. Polyurethanes are the 5th most produced polymer worldwide, as shown in Figure 1.[6] Of the global production of polyurethanes, petroleum-based polyurethanes account for 14,000 kton. The bio-based polyurethane market (polyols from renewable resources combined with petroleum isocyanates) is comparatively small at 28 kton.[6]

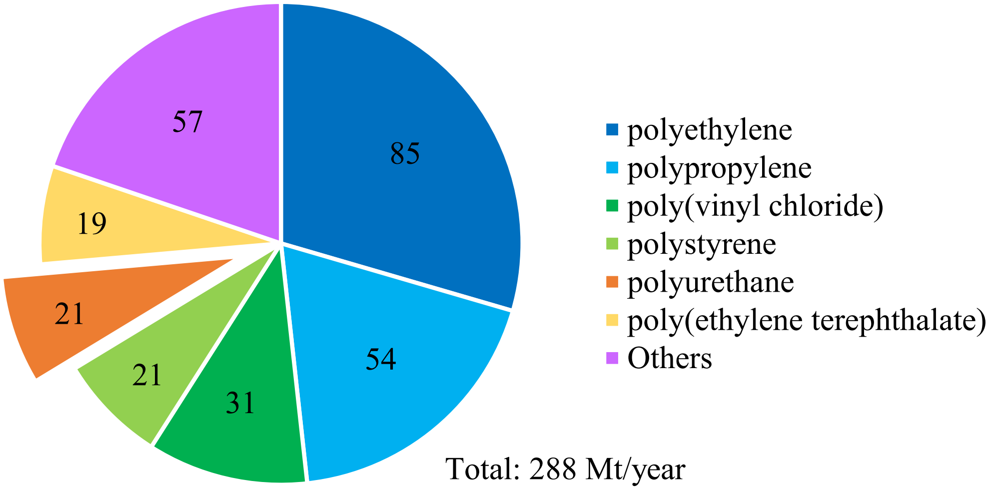


*Figure 1: Estimated plastics production worldwide for 2012. 'Others' include polyamides and synthetic rubbers.*[6]

Besides trying to reduce the global consumption of petroleum, another driving force for bio-based polyurethanes is to reduce hazardous synthesis methods. Isocyanates are toxic if inhaled, and therefore undesirable in industrial scale polyurethane manufacturing.[7] For example, the isocyanate: methyl isocyanate, was responsible for the 1984 Bhopal disaster.[3] Isocyanates are industrially produced using the toxic gas phosgene, which was used as a chemical weapon in WWII.[8] Polyurethanes can also be produced through alternate pathways without the use of isocyanates, and these can be fully bio-based.[9]

Many researchers have developed bio-based polyols from feedstocks of natural oils and chemical companies are starting to commercialize bio-based polyols on a large scale.[10-14] Although less common, processes yielding bio-based isocyanates have been published as well.[15-17] Cases of polyurethanes synthesized using bio-based polyols and petroleum derived isocyanates are common, however there is limited research completed on using both bio-based polyols and isocyanates to synthesize polyurethanes.[18]

Adfast Corp., Canada's largest supplier of commercial adhesives and sealants, has partnered with McGill University on this research venture to develop a new polyurethane formulation using renewable feedstocks. Their wide range of products are used throughout homes and commercial buildings on roofing, windows, floors, etc. While their adhesives are popular in construction, they are also gaining attention across the transportation industry. For example, adhesives are becoming more popular than traditional metallic fasteners in transport trucks due to their increased durability and aerodynamic benefits.

The polyurethane formulation currently used by Adfast combines a 4,000 g/mol poly(propylene glycol) (PPG) and isophorone diisocyanate (IPDI). The reaction mechanism for forming polyurethanes from PPG and IPDI is shown below in Figure 2.[19] The –OH end group, found on both ends of the polyol, forms a urethane linkage when reacted with an isocyanate.

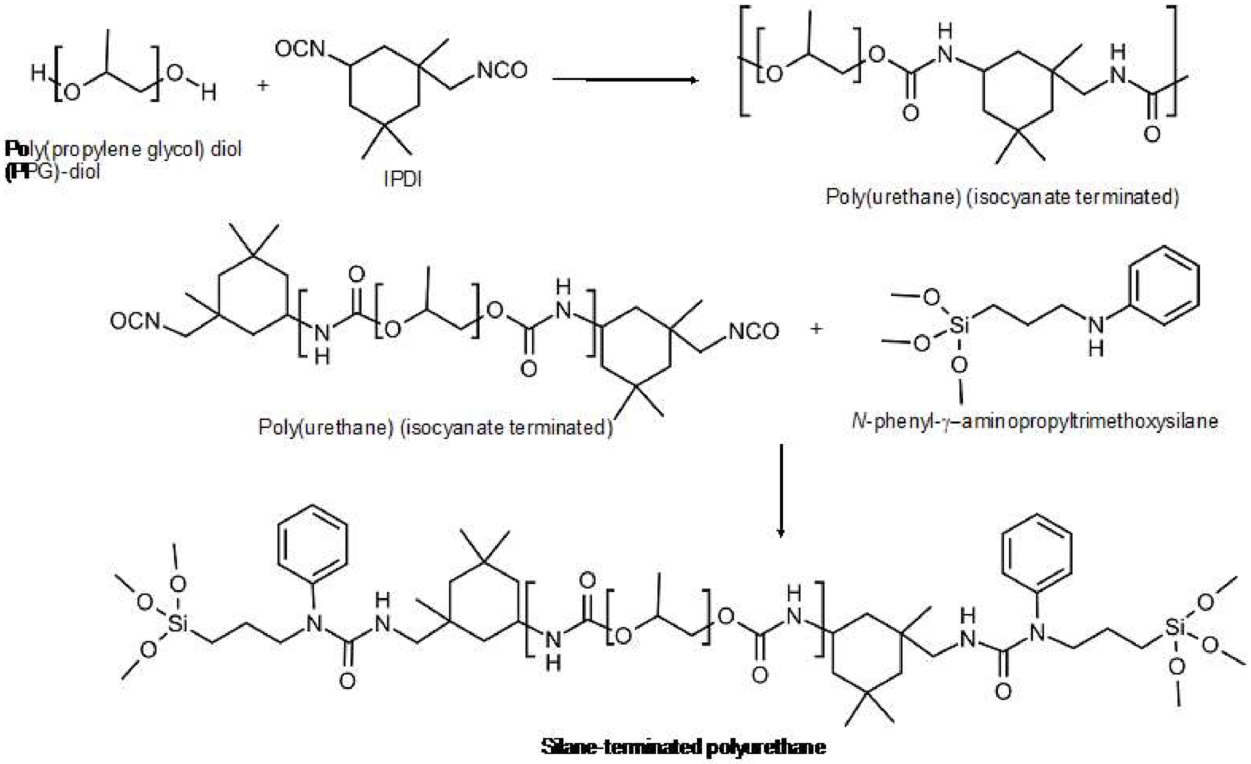


*Figure 2: Mechanism for addition of PPG and IPDI with silane end-capper to synthesize hybrid polyurethanes.*[19]

Before adding the IPDI to the PPG, a water scavenger, 4-methyl-benzenesulfonylo isocyanate, is added to the polyol. It is necessary to react any moisture in the polyol with this water scavenger first so that the IPDI does not react with water. When an isocyanate reacts with water, an amine and carbon dioxide are formed. This is the reaction mechanism responsible for the production of PU foams[10], however it is not desired in the synthesis of PU adhesives. The reaction between the PPG and IPDI is driven by an organotin catalyst, Fascat® 4202 (Dibutyltin dilaurate: $Sn(C_4H_9)_2(COOC_{11}H_{23})_2$). After three hours of reaction, the silane end-capper, N-phenyl γ-aminopropyltrimethoxysilane, is added, terminating the polymerization reaction. The silane end-capper allows for curing of the polyurethane through reaction of the labile trimethoxysilane groups with atmospheric moisture. Adfast's formulation uses an excess of IPDI to achieve a product with the desired physical properties.

## 1.1 OBJECTIVES

This thesis covers three main objectives: 1) the characterization of Adfast's original product and the measurement of benchmark properties, 2) the incorporation of bio-based polyols in the place of the original petroleum based polyol, and 3) the incorporation of a bio-based isocyanate into the formula as well, to produce a fully bio-based polyurethane.

While this thesis project focuses on developing a bio-based product for Adfast with the same key characteristics as the current product, the first step (Objective 1) was to provide the framework for analysis of the current product using techniques available in the Maric labs ($^1$H-NMR, GPC) which can then be used as benchmarks for succeeding products. The initial phase of the thesis project was to characterize the polyurethane that is currently formulated at the Adfast facility. In order to replicate Adfast's product, a small scale reactor was set up to simulate the industrial process. Using the formulation provided, the polyurethane product was synthesized on a small scale (~30 mL) and characterized. The product was compared to samples of Adfast's product using Fourier-transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC) and they were concluded to be the same product. This polyurethane was characterized, and the analysis was shared with Adfast in order to help them troubleshoot their current product.

The second step of this project was to incorporate a selection of bio-based polyols into the formula in the place of the 4,000 g/mol PPG polyol (Objective 2). The Maric lab received samples of commercial bio-based polyols from GC Innovation America and Sovermol® (a subsidiary of BASF). The polyols were characterized and compared to the 4,000 g/mol PPG polyol that Adfast currently uses. Adfast's formula was adjusted to account for the different molecular weights and functionalities of the bio-based polyols and polyurethanes were synthesized using bio-based polyols and the original isocyanate IPDI. The resulting polyurethanes were characterized and the effect of using the different grades of bio-based polyols was assessed. Key physical properties (viscosity and stress-strain properties) were measured for the different polyurethane formulations.

Based on the promising properties of one formulation using a bio-based polyol, Myrinol™ DG-110 (from GC Innovation America), a bio-based isocyanate, ethyl ester L-lysine diisocyanate (LDI, derived from the amino acid L-lysine), was also incorporated into the formulation (Objective 3). The properties of this resin were assessed and compared to those of Adfast's original resin.

This system was investigated further, and it was found that catalyst was not needed to drive the reaction. The properties of this bio-based PU were found to be similar to the original IPDI/PPG PU produced by Adfast.

Future work for this project includes the economic assessment of the bio-based formulations presented here and further testing and optimization in order to determine if a bio-based polyurethane can be compatible with Adfast's products. Based on the viscosity and stress-strain properties, both the IPDI/Myrinol™ DG-110 and LDI/Myrinol™ DG-110 PU formulations show promise, however there are limitations in terms of scale-up for both of these formulations, and many other properties that must be assessed before either can be incorporated into a commercial product.

# 2.0 LITERATURE REVIEW

## 2.1 POLYURETHANE CHEMISTRY

Polyurethanes were first synthesized by Otto Bayer in 1937.[20] Today, the same method that Bayer used originally is still the most commonly used: the reaction between an isocyanate and a polyol. Polyols are compounds that contain two or more hydroxyl groups.[21] Based on the number of hydroxyl groups per molecule, called the functionality of the molecule, polyols can be classified as diols (having two hydroxyl groups per molecule), triols (having three hydroxyl groups per molecule) etc.[10] Polyols for polyurethane reactions can generally be classified as polyether polyols or polyester polyols. Polyester polyols are used in foam applications while polyether polyols are mainly used for thermoplastics and elastomers.[19] As of 2012, the polyol market consisted mostly of polyester polyols (69%) with polyether polyols making up 19%.[22] Polyurethanes were the 6th most used polymer globally as of 2006, having a global production of 14 Mt.[12]

Isocyanates are defined as molecules containing an N=C=O group and can be aromatic or aliphatic. In general, aromatic isocyanates exhibit greater reactivity due to the electron attracting hydrocarbon group. Due to the difference in reactivity, aromatic isocyanates are mostly used for foams while aliphatic isocyanates are more commonly applied in coatings and adhesives.[10] In general, aromatic isocyanates produce more brittle resins and aliphatic isocyanates produce chains with more elasticity.[23] Polyurethanes from aliphatic isocyanates are more resistant to UV radiation and degrade at a slower rate, making them more appropriate for applications that will be exposed to sunlight.[23] Isocyanates are most commonly synthesized from primary amines through phosgenation followed by dehydro-halogenation.[10] Phosgenation is the only method of synthesizing isocyanates that is currently used on an industrial scale. Phosgenation involves dissolving amines in a solvent and then treating with phosgene to produce isocyanates.[24] Polyurethanes have also been synthesized without the use of isocyanates, using alternate reaction mechanisms. This is an attractive option as it eliminates isocyanates and phosgene, both toxic, from the process. Cyclic carbonates can be reacted with polyfunctional amines to produce polyurethanes, and both of these molecules can be bio-based.[9, 25] Non-isocyanate polyurethanes will be covered further in following sections of this thesis.

When combined, the isocyanate group and the hydroxyl group of the polyol form a urethane linkage (NHCOO).[19] The general reaction mechanism for the polyaddition reaction between a diisocyanate and a polyol with two hydroxyl groups (a diol) is shown below in Figure 3.

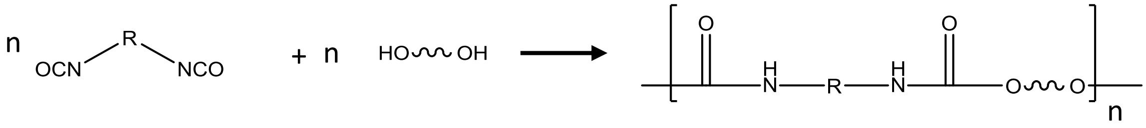


*Figure 3: Polyurethane synthesis from a diol and a diisocyanate.*

Depending on the functionality of both the polyol and the isocyanate, the resulting polyurethane will have different properties. When the polyol and isocyanate both have a functionality of two, in the case of Adfast's original formulation, the polyurethane will be linear in structure. Cross-linking or branching of the polyurethane will occur if either the polyol or isocyanate has a functionality of three or greater.[10] Segmented polyurethanes can be formed using polyols and diisocyanates. Segmented polyurethanes contain both rigid and soft segments: the polyol typically forms the soft segment and the diisocyanates the hard segment (Figure 4). The proportion of soft and hard segments can be controlled to produce a product with the desired characteristics.[26]

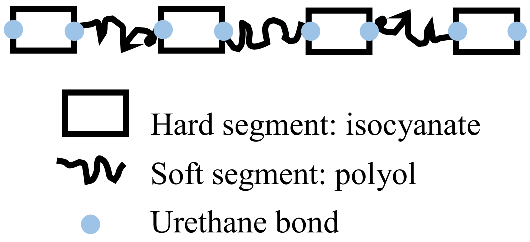


*Figure 4: Graphical explanation of segmented polyurethanes.*

## 2.2 BIO-BASED POLYOLS

Vegetable oils are the primary feedstock for bio-based polyols.[21] Vegetable oils are triglycerides, meaning they are made of molecules containing three fatty acids (see Figure 5). The most common fatty acids found in vegetable oils are palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid.[27] The structures of these common acids are shown in Figure 6. Castor oil, a non-edible oil, contains ricinoleic acid which has naturally occurring hydroxyl groups.[28]

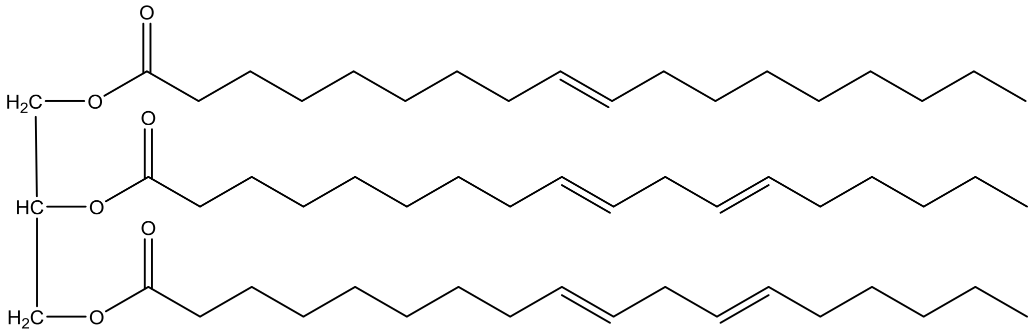


*Figure 5: Structure of a typical triglyceride.*

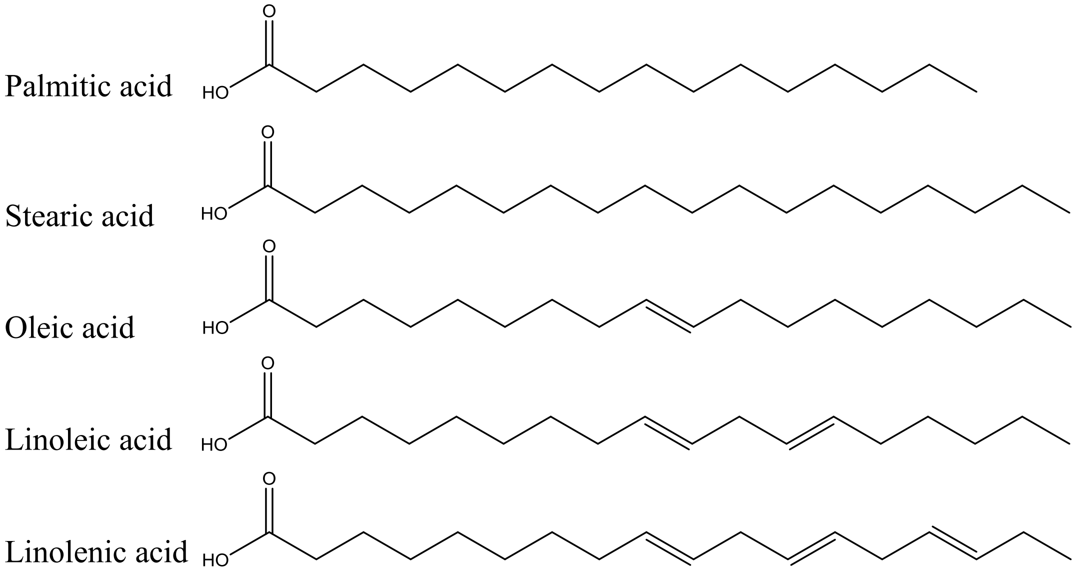


*Figure 6: Structures of common fatty acids.*

In 2012, 156 million tons of vegetable oils were produced.[29] Of this annual production 75% was used for food and most of the remainder went towards industrial applications including fuels and chemicals such as polyols.[30] In terms of large scale synthesis, soybean, palm and rapeseed oils are the most logical in terms of price.[30] For North American research and applications, soybean oil is the most attractive natural oil as 60% of the world's soybean oil is produced in the United States.[30]

Five methods are currently being used to experimentally derive polyols from vegetable oils: 1) epoxidation and oxirane ring-opening, 2) hydroformylation and hydrogenation, 3) ozonolysis, 4) thiol-ene coupling, and 5) transesterification/amidation.[10] These methods use either the double carbon bond or the ester moieties of vegetable oils to transform them into polyols.

Epoxidation occurs at the double carbon bond of vegetable oils. Using a protic compound such as an alcohol, acid, or water, epoxidation followed by oxirane ring-opening can produce a polyol. Vegetable oils with more unsaturation, (i.e. more double carbon bonds), will produce polyols with higher functionalities. Consequentially, the more functional a polyol is, the more viscous it tends to be. Polyols produced by this method using inorganic acids are generally waxes at room temperature.[31] Today, epoxidation with oxirane ring-opening is the most common method used for the synthesis of bio-based polyols. It is widely used and patented due to the variety of nucleophiles that can be used in the reaction.[12]

During hydroformylation of vegetable oils, double bonds are transformed into aldehydes using catalyzed syngas. These aldehydes are then converted to hydroxyl groups via hydrogenation. One hydroxyl group is formed for every double bond of the original vegetable oil, meaning that the functionality of the polyols will be the same as that of the vegetable oils.[32] Currently, two industrial scale processes for the hydroformylation of natural oils have been used. Dow Chemical Company used hydroformylation to synthesize their Renuva™ product from soybean oil. Dow has recently discontinued their Renuva™ product due to a high variability in the double bond composition of the fatty acids.[12] BASF also used hydroformylation for its Lupranol® Balance product.[11]

In order to use ozonolysis to produce a polyol from vegetable oil, two steps are followed. First, an ozonide is formed at the double bond and is decomposed into an aldehyde and carboxylic acid. The aldehyde is then reduced into an alcohol using a catalyst. While epoxidation and hydroformylation produce polyols with hydroxyl groups in the middle of their chains, ozonolysis results in a hydroxyl group at the end of the chain. This leads to faster curing and allows for more crosslinking.[33]

Thiol-ene coupling employs UV irradiation to graft thiols onto the double bonds of fatty acids.[34] Although using UV radiation is used most commonly with vegetable oils, heat-initiation of the reaction is also possible but results in a longer reaction time.[10] Thiol-ene coupling has been noted in literature to synthesize bio-based polyols from both rapeseed oil and soybean oil.[34, 35]

While the four methods discussed above take place at the fatty acid double bond, transesterification occurs using the ester moiety of vegetable oils. Most commonly, glycerol is used with a small amount of soap and a basic catalyst to create glycerides. All resulting hydroxyl groups will be located along the chain, meaning that polyols synthesized using transesterification will make more flexible polyurethanes when combined with isocyanates.[30]

While natural oils such as soybean and sunflower do not contain hydroxyl groups, one of the five methods above is commonly used to add the necessary hydroxyl groups to create a polyol. Castor oil naturally contains hydroxyl groups, found in the ricinoleic acid molecule (see Figure 7) which makes up approximately 90% of castor oil. Castor oil can either be modified using transesterification or amidation in order to increase the functionality but it can also be used as it exists naturally to produce polyurethanes.[27]

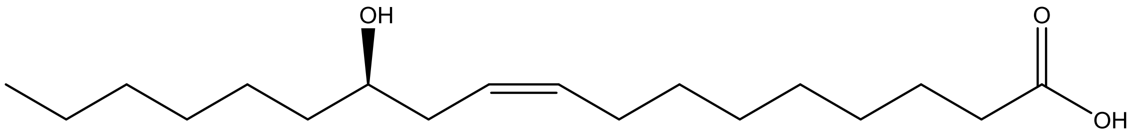


*Figure 7: Molecular structure of ricinoleic acid.*

In addition, polyols have been derived from biomass through oxypropylation.[1] This method uses waste biomass rather than food oils, making it more attractive in terms of a green chemistry perspective. Succinic acid has also been investigated as a starting material to produce polyols. Succinic acid is conventionally produced through hydrolysis of maleic anhydride, a petrochemical product[6], but it can also be produced via fermentation of sugars giving bio-succinic acid. As of 2013 there was an estimated annual global market of 40 kton of succinic acid, in which 1kton (2.5%) was bio-based.[6] This is a promising process as $CO_2$ is consumed by microorganisms during succinic acid production[36], an additional green aspect. GC Innovation America has developed several grades of commercial polyols based on bio-derived succinic acid under the name Myrinol™. Bio-succinic acid is combined with a petroleum-based diol, such as diethylene glycol or 1,4-butanediol, to form polyols that are 40-66% bio-based as seen in Figure 8.[37]

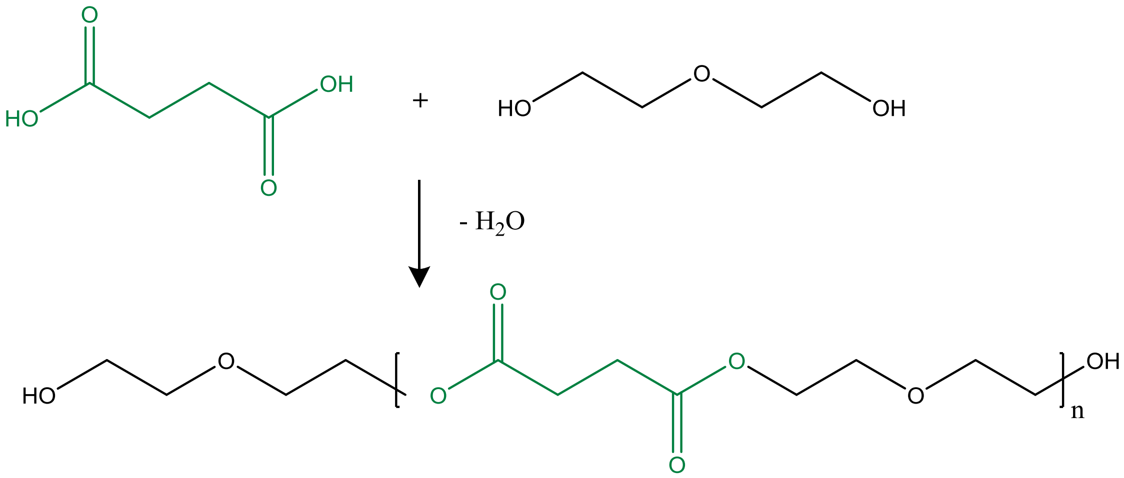


*Figure 8: Synthesis of a Myrinol™ polyester polyol from bio-succinic acid.*

Multiple commercial bio-based polyols are available today (see Table 1 for summary), and most are synthesized through epoxidation of various vegetable oils. Agrol®, a range of products developed by Biobased Technologies, are soybean oil-based polyols with a renewable content of 96%.[12] The double bond of the soybean oil is first epoxidized using peroxy acid, and then undergoes a ring opening.[38] The Agrol® line of products includes one polyol, Agrol® Diamond, which, in addition to epoxidation and ring opening, undergoes aminolysis of the ester functions using an alcohol amine.[39] This leads to the Agrol® Diamond product having a higher hydroxyl index compared to the rest of the Agrol® product line.[12]

Cargill has developed a bio-based polyol, BiOH®, also derived from soybean oil.[12] Cargill uses epoxidation followed by ring opening using methanol with a fluoroboric acid catalyst to synthesize polyols.[13] These polyols contain secondary alcohols only and have no double bonds which gives greater thermal stability. BiOH® polyols are used in polyurethane foam applications and have a renewable carbon content of 95%.[12] Cargill claims that for every 1 million pounds of bio-based polyols used, approximately 2,200 barrels of crude oil can be saved.[40] Additionally, Cargill's process for soy-based polyols requires less energy than a traditional polyol synthesis process.[40]

BASF has a wide range of polyols available that are derived from various vegetable oils.[12] These polyols, under the name of Sovermol®, are synthesized by epoxidation of vegetable oils followed by ring opening using an alcohol. The resulting hydroxylated oil then undergoes transesterification using the same alcohol to form the polyol.[14]

*Table 1: Summary of commercial bio-based polyol properties.*

| Company | Product | Functionality | OH # (mg KOH/g) | Viscosity (cP) | Bio-Based Content (%) |
|---|---|---|---|---|---|
| Agrol®[12] | Agrol® 2.0 | 2.0 | 65-75 | 230 | N/A |
| | Agrol® Diamond | 3.0 | 320-350 | 3,400 | N/A |
| Cargill BiOH®[12] | BiOH® X-0500 | 2.0 | 56 | 4,500 | N/A |
| | BiOH® X-0210 | 4.4 | 235 | 8,900 | N/A |
| BASF Sovermol®[41] (See Appendix A) | Sovermol® 830 | 2.6 | 241 | 875 | 80-100 |
| | Sovermol® 908 | 2.0 | 206 | 2,300 | 80-100 |
| GC Innovation America[42] | Myrinol™ DG-110 | 2.0, linear | 113 | 440 (60°C) | 50 |
| | Myrinol™ EG-110 | 2.0, linear | 107 | 400 (80°C) | 66 |
| | Myrinol™ HD-110 | 2.0, linear | 108 | 450 (60°C) | 40 |
| | Myrinol™ DGTA-56 | ~2.4, branched | 61 | 3,150 (60°C) | 47 |
| | Myrinol™ DGTB-56 | ~2.7, branched | 64 | 5,000 (60°C) | 47 |

## 2.4 BIO-BASED ISOCYANATES

While extensive research has been conducted on producing polyols from natural resources, limited cases of bio-based isocyanates are available.[10] Most polyurethanes that have been produced from bio-based polyols have used petroleum-based isocyanates.[15, 18, 43] Finding alternatives to traditional petroleum based isocyanates synthesized through phosgenation is a priority of researchers due to the toxicity of phosgene.[10]

Three well-known methods of producing isocyanates without phosgene exist: via Curtius rearrangement, Hofmann rearrangement and Lossen rearrangement (see Figure 9).[17, 44] All three of these reactions include an intermediate product of nitrenes, making them unsuited for scale-up.[5, 17] The Curtius rearrangement also involves azides which are hazardous at a large scale due to their explosive properties.[15]

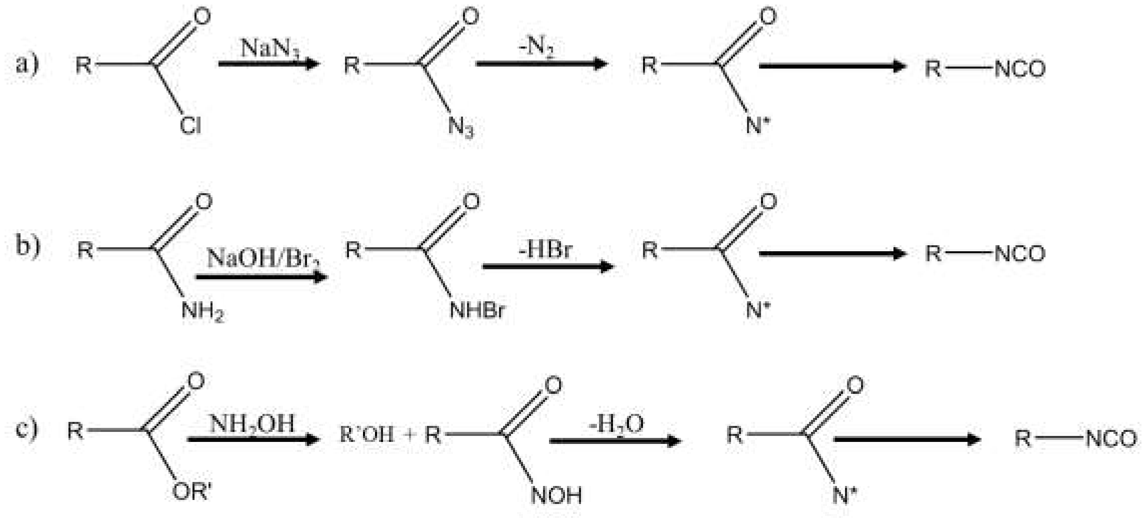


*Figure 9: Laboratory scale synthesis of isocyanates: a) Curtius, b) Hoffman and c) Lossen rearrangements.*

The production of a diisocyanate from fatty-acids is reported in a U.S patent.[16] Using hydrogenated dinitrile compounds, diamine precursors were prepared and then used to synthesize diisocyanates. Diisocyanates have been created from isosorbides through double esterification with succinic anhydride.[18] An isocyanate has been produced from soybean oil by substituting the allylic bromides of the oil with AgNCO.[17] The Curtius rearrangement has been used to synthesis oleic-acid based diisocyanates on a lab scale. Using this fatty-acid based isocyanate and a lipid-based polyol it was shown that it was possible to produce an entirely bio-based polyurethane.[15] The diisocyanate, L-lysine diisocyanate (LDI) has been derived from L-lysine amino acid and has been used to synthesize non-toxic biodegradable polyurethanes.[45-47] LDI is an attractive option for bio-medical PU applications as its degradation products are ethanol and L-lysine, both which are biocompatible. Dimeryldiisocyanate (DDI), synthesized from fatty acids, has also been used to create fully renewable polyurethanes.[43] One commercial bio-based isocyanate that is available is a fatty-acid based diisocyanate (dimer diisocyanate) from Henkel Corporation Company and General Mills.[27]

## 2.5 NON-ISOCYANATE POLURETHANES

While this thesis focuses on creating polyurethanes from bio-based polyols and diisocyanates, it will lead to subsequent projects looking into bio-based non-isocyanate polyurethanes. Non-isocyanate polyurethanes (NIPUs) are attractive as the common isocyanates used for polyurethane synthesis (methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI)) have been found to be toxic.[48] Isocyanates are a leading cause of occupational asthma, not only from inhalation but also from skin exposure.[49] Fully cured polyurethanes formed using isocyanates have no health concerns, but the exposure to isocyanates that industrial plant workers face is a concern.[7]

The traditional synthesis of isocyanates also involves phosgene, which is a highly toxic gas. Non-isocyanate polyurethanes present a greener alternative by completely eliminating exposure to both isocyanates and phosgene.[50] In addition to relying on renewable resources rather than petroleum and having safer process conditions for workers, non-isocyanate polyurethanes are not as sensitive to moisture as traditional polyurethanes are.[51]

Four methods of synthesizing NIPUs have been reported in literature: polycondensation, polyaddition, rearrangement[52, 53], and ring opening polymerization[54, 55]. Of these four methods, polyaddition is the most attractive option as there are no isocyanates, phosgene or other harmful chemicals involved in the reaction.[56] The issue with the polyaddition mechanism is that cyclic carbonates are not widely available commercially.[57] Thiol-ene addition has also been used to synthesize non-isocyanate polyurethanes by way of a urethane monomer containing both thiol and -ene functional groups.[48]

Research efforts have also been focused on combining NIPU chemistry with carbon dioxide fixation. Using catalytic copolymerization of carbon dioxide with oxiranes, aliphatic carbonates can be synthesized. Using a ring opening polymerization with di- and poly-amines, these carbonates can form non-isocyanate polyurethanes.[55] Terpenes, ester-free and highly unsaturated molecules have been investigated for the production of dicarbonates. Limonene, a waste product from citrus fruits, can be transformed into carbonates and allows for more carbon fixation than traditional natural oil feedstocks.[58] Amines can also be derived from biological materials, and have been combined with bio-based carbonates to form completely bio-based NIPUs.[9] Other than ring-opening of cyclic carbonates by amines, the other most cited method of forming non-isocyanate polyurethanes is self-condensation of AB monomers containing both hydroxyl and acyl azide groups.[53]

Both polyurethanes from bio-based polyols and isocyanates, and non-isocyanate polyurethanes are of interest to Adfast and McGill. Bio-based PUs based on polyols and diisocyanates could provide Adfast with a fully bio-based product. This is desirable to stay relevant in the market as bio-based plastics become more popular and the world's reliance on petroleum products decreases. This route is limited by the difficulty of scaling-up the synthesis of bio-based isocyanates. NIPUs, which can also be completely bio-based, offer the additional advantage of eliminating the hazard of the toxicity of isocyanates. NIPUs also come with the challenge of scale-up, which has not been explored in detail. The main factor limiting the scale-up of NIPUs is the lack of commercial suppliers of carbonates.[57]

Currently, since the polyol makes up the majority of the mass of Adfast's formulation, developing PUs from bio-based polyols and petroleum-based isocyanates is of immediate interest to Adfast. While this thesis focusses on the synthesis and characterization of polyurethanes from bio-based polyols and petroleum isocyanates, and one case of a bio-based polyol with a bio-based isocyanate, the results will be useful when developing further PUs for sealant applications. The benchmark properties of Adfast's original IPDI/PPG resin will be used as a comparison for future NIPUs as well as additional bio-based polyol/diisocyanate systems.

## 3.0 EXPERIMENTAL

### 3.1 MATERIALS

Poly(propylene glycol) (PPG, >95%, Bayer), 4-methyl-benzenesulfonylo isocyanate (L.V. Lomas), isophorone diisocyanate (IPDI, 99.8%, Vestanat®, Evonik), Fascat® 4202 catalyst (>95%, Arkema), N-phenyl $\gamma$-aminopropyltrimethoxysilane (60-100%, GE Canada), and Reaxis® C417VM (55-65% dioctyltin oxide, 35-45% trimethoxy(vinyl) silane, >5% methanol) were kindly provided by Adfast and were used as received. The sample of 1.7 mol IPDI/mol PPG PU resin used as a standard (for FTIR and GPC analysis) was provided by Adfast.

Tetrahydrofuran (THF, 99.9% HPLC grade), used as the solvent for GPC analysis, was received from Fisher Scientific. Deuterated chloroform ($CDCl_3$, 99.8%), used as the solvent for $^1$H-NMR was obtained from Cambridge Isotopes Laboratory.

Two different bio-based polyols were received from Sovermol®: Sovermol® 830 and Sovermol® 908. One grade of polyol, Myriant™ DG-110, was received from Myriant™. After this material was received, Myriant™ changed their name to GC Innovation America, and the Myriant™ DG-110 polyol was renamed Myrinol™ DG-110. According to the new data sheet, all product specifications are the same. For the remainder of this thesis, the polyol will be referred to as Myrinol™ DG-110. All polyols were used as received without further purification.

Ethyl ester L-lysine diisocyanate (LDI, 97%) was purchased from Alfa Aesar (through Thermo Fisher Scientific).

### 3.2 SYNTHESIS

All polyurethane reactions were conducted in a 100 mL three-necked round-bottom glass flask (with the exception of the LDI/Myrinol™ DG-110 syntheses which were conducted in a 50 mL round-bottom flask) equipped with an overhead reflux condenser connected to the second neck. The flask was placed in a heating mantle which was held on a magnetic stir plate. A magnetic stir-bar with a high energy magnet, specially designed for high viscosity materials, was used. After the addition of the polyol, the system was sealed and an ultrapure nitrogen atmosphere was introduced (nitrogen needle was inserted through a rubber septum in the third neck of the reactor) and held for the duration of the reaction. A needle was inserted into the top of the overhead condenser to vent the nitrogen purge. The thermocouple was inserted into the first neck of the reactor through a rubber septum. The magnetic stir bar was turned on and used throughout the entire reaction. When synthesizing the bio-based PUs, the stirring rate was continuously adjusted to ensure adequate stirring when the reaction media was very viscous. An ethylene glycol/reverse osmosis water (30/70 vol%) mixture was supplied to the condenser from the chiller (Fisher Scientific Isotemp 3016D Digital Refrigerated Bath) at 5°C.

With the exception of the polyols, which were measured into the reactor gravimetrically, all reactants were added using syringes directly into the reactor through the rubber septum due to their hazardous nature. The addition volumes were calculated based on the densities of the materials. Samples were taken throughout the reaction by briefly removing the rubber septum and taking a small amount of resin from the reactor with a metal spatula (as the resin was too viscous to use a syringe to remove samples). The rubber septum was then replaced immediately after the sample was extracted in order to maintain the inert atmosphere. The same addition process (see Table 2) was performed for all formulas, except for those which were performed without the use of catalyst (Step 4, Table 2), in which the catalyst addition was simply skipped. For the curing tests performed, Step 6 (Table 2) was followed after the completion of the one-hour end-capping reaction.

*Table 2: Reaction steps in polyol/isocyanate polyurethane synthesis.*

| Step | Actions | Time | Reactor Temperature |
|---|---|---|---|
| 1 | Weigh polyol into reactor using scale. Seal reactor, start nitrogen flow, start condenser, start magnetic stir bar. | ~10 minutes | ~21°C (room temperature) |
| 2 | Add 4-methyl-benzenesulfonylo isocyanate (water-scavenger) to reactor using reusable 1.0 mL syringe through rubber septum. | 10 minutes | ~21°C (room temperature) |
| 3 | Add isocyanate to reactor using disposable syringe through rubber septum. Increase temperature to 45°C. | 10 minutes | 45°C |
| 4 | Addition of Fascat ® 4202 catalyst to reactor using reusable 1.0 mL syringe. Increase temperature to 65°C. | 3 hours | 65°C |
| 5 | Addition of silane end-capper using disposable syringe through rubber septum. | 1 hour | 65°C |
| 6 | Addition of Reaxis® C417VM using reusable 1.0 mL syringe through rubber septum. | ~3 minutes | 65°C |

In total, 11 differing polyurethane resins were synthesized, characterized, and their physical properties tested. Five different molar ratios of IPDI/PPG PUs were synthesized using the reactants as listed in Table 3. Additionally, six resins were synthesized using bio-based polyols in the place of the PPG polyol. The latter two of these six formulas used the bio-based isocyanate, LDI. These formulas are detailed in Table 4. At the end of the three-hour reaction time, the reactions were ceased by stopping the stir bar, removing the reactor from the heating mantle and then pouring the resin out while still warm. Measurement of viscosity was performed immediately following the removal of the resin from the reactor (letting the resin cool to room temperature as it was transferred from the reactor to the rheometer). In order to form tensile bars, the resin was poured directly from the reactor while still warm into silicone tensile bar molds where it was left to cure over time (~15 days) at atmospheric conditions.

*Table 3: Reaction formulas for IPDI/PPG PU resins in mol%.*

| Formula | Polyol | Water Scavenger | Isocyanate | Catalyst | Silane End-capper |
|---|---|---|---|---|---|
| 1.4 mol IPDI/mol PPG | PPG, 28.10% | 4-methyl-benzenesulfonylo isocyanate, 5.70% | IPDI, 39.29% | Fascat® 4202, 0.08% | N-phenyl γ-aminopropyltrimethoxysilane, 26.84% |
| 1.7 mol IPDI/mol PPG | PPG, 23.64% | 4-methyl-benzenesulfonylo isocyanate, 4.80% | IPDI, 41.14% | Fascat® 4202, 0.07% | N-phenyl γ-aminopropyltrimethoxysilane, 30.34% |
| 2.0 mol IPDI/mol PPG | PPG, 21.32% | 4-methyl-benzenesulfonylo isocyanate, 4.33% | IPDI, 42.78% | Fascat® 4202, 0.06% | N-phenyl γ-aminopropyltrimethoxysilane, 31.51% |
| 2.5 mol IPDI/mol PPG | PPG, 17.86% | 4-methyl-benzenesulfonylo isocyanate, 3.62% | IPDI, 45.16% | Fascat® 4202, 0.05% | N-phenyl γ-aminopropyltrimethoxysilane, 33.31% |
| 3.0 mol LDI/mol PPG | PPG, 15.39% | 4-methyl-benzenesulfonylo isocyanate, 3.12% | IPDI, 46.98% | Fascat® 4202, 0.05% | N-phenyl γ-aminopropyltrimethoxysilane, 34.46% |

*Table 4: Reaction formulas for bio-based polyol PU resin in mol%.*

| Formula | Polyol | Water Scavenger | Isocyanate | Catalyst | Silane End-capper |
|---|---|---|---|---|---|
| 1.7 mol IPDI/mol Sovermol® 830 | Sovermol® 830, 20.27% | 4-methyl-benzenesulfonylo isocyanate, 0.04% | IPDI, 45.85% | Fascat® 4202, 0.01% | N-phenyl γ-aminopropyltrimethoxysilane, 33.83% |
| 1.7 mol IPDI/mol Sovermol® 908 | Sovermol® 908, 24.83% | 4-methyl-benzenesulfonylo isocyanate, 0.09% | IPDI, 43.21% | Fascat® 4202, 0.01% | N-phenyl γ-aminopropyltrimethoxysilane, 31.86% |
| 1.7 mol IPDI/mol Myrinol™ DG-110 | Myrinol™ DG-110, 24.85% | 4-methyl-benzenesulfonylo isocyanate, 0.04% | IPDI, 43.21% | Fascat® 4202, 0.03% | N-phenyl γ-aminopropyltrimethoxysilane, 31.88% |
| 1.7 mol IPDI/mol Myrinol™ DG-110 | Myrinol™ DG-110, 24.85% | 4-methyl-benzenesulfonylo isocyanate, 0.04% | IPDI, 43.22% | N/A | N-phenyl γ-aminopropyltrimethoxysilane, 31.89% |
| 1.7 mol LDI/mol Myrinol™ DG-110 | Myrinol™ DG-110, 36.01% | 4-methyl-benzenesulfonylo isocyanate, 0.18% | LDI, 63.70% | Fascat® 4202, 0.11% | N/A |
| 1.7 mol LDI/mol Myrinol™ DG-110 | Myrinol™ DG-110, 24.83% | 4-methyl-benzenesulfonylo isocyanate, 0.13% | LDI, 63.70% | N/A | N-phenyl γ-aminopropyltrimethoxysilane, 31.85% |

### 3.3 CHARACTERIZATION

FTIR (Spectrum BX, Perkin-Elmer) was used to verify the composition and estimate the NCO content of the PU resins. The peak heights were measured using Spectrum software. A calibration curve (Figure 10) was produced in order to quantify the amount of free NCO in the PU resin throughout the reaction. Known concentration samples of IPDI in PPG (5-70 mol%) were tested using FTIR, and a relationship was found between the concentration of NCO end-groups and the intensity of the FTIR spectra NCO peak transmittance (~2270 cm$^{-1}$).

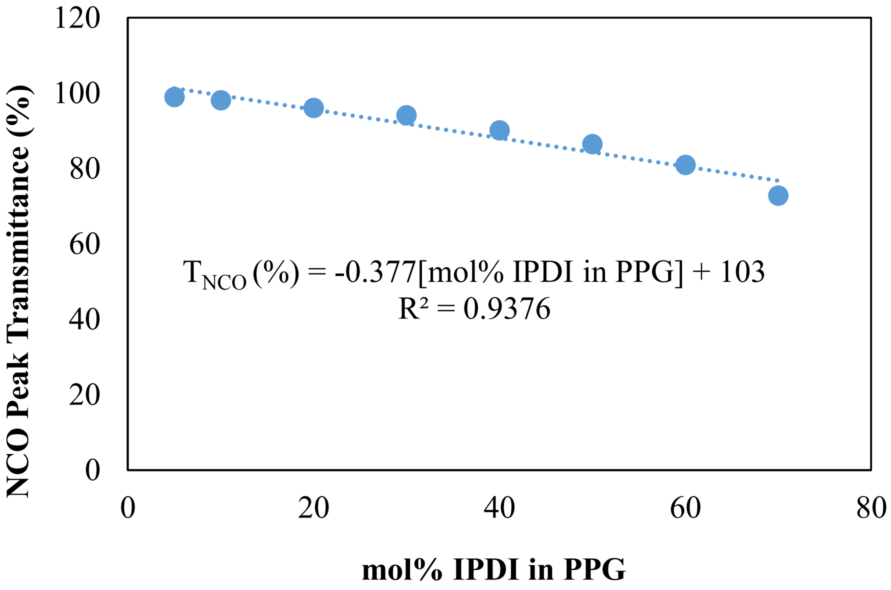


*Figure 10: Calibration curve for determining NCO content (mol%) from NCO peak height (% transmittance).*

The number-average molecular weights ($M_n$, GPC) and the molecular weight distributions (Đ = $M_w/M_n$) were measured using gel permeation chromatography (GPC, Water Breeze). HPLC grade tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 0.3 mL/min. The GPC was equipped with three Waters Styragel HR columns (HR1 with a molecular weight measurement range of $10^2 - 5 \times 10^3$ g/mol, HR2 with a molecular weight measurement range of $5 \times 10^2 - 2 \times 10^4$ g/mol, and HR4 with a molecular weight measurement range of $5 \times 10^3 - 6 \times 10^5$ g/mol), and a guard column. During the analysis the columns were heated to 40°C. A differential refractive index (RI 2414) detector was used. The $M_n$ values for all PU resins and raw materials were determined by calibration with 10 linear narrow molecular weight distribution P(MMA) standards (Varian Polymer Standards, molecular weights ranging from 875 to 1,677,000 g/mol).

The structures of the bio-based polyols were determined using a Varian NMR Mercury spectrometer ($^1$H-NMR, 300 MHz, 32 scans) using $CDCl_3$ deuterated solvent.

A strain-controlled rheometer (Anton Paar MCR 302, Anton Paar Canada, St-Laurent, QC, Canada) with parallel plate geometry (25 mm plate diameter) was used to measure the viscosities of the resins. Disposable sets of parallel plates were used as the resins were of high viscosity and the disposable plates allowed for easier cleaning. Disposable plates were also used so that in cases where the resin cured to the plate, the plate could be disposed of after the test. PU resin viscosity was measured using steady shear, with a shear rate from 0.1 1/s to 10 1/s using a 1.0 mm gap measuring position. This shear rate range is within the linear viscoelastic regime. An average viscosity over the shear rate is reported. Polyol viscosity was measured using steady shear, with a shear rate from 0.1 1/s to 1,000 1/s using a 1.0 mm gap measuring position. A DMTA curing test with 0.05% strain and a frequency of 1 Hz, was used to calculate the storage modulus (G′) and loss modulus (G") over time to estimate the gel time, and curing time of the PU resin. Anton Paar Rheoplus software (RHEOPLUS/32 version 3.61, Anton Paar Germany, Ostfildern, Germany, 2011) was used to perform both the viscosity and curing time tests. All rheology measurements were conducted at room temperature (~20°C).

The stress-strain properties of the cured PU resins were measured using a Shimadzu EZ Test testing system at room temperature and a cross-head speed of 15 mm/min. Dog-bone style tensile specimens were made using a silicone mold (ASTM D638, type V, overall length = 63.5 mm, overall width = 9.53 mm). The width and thickness of each sample was measured with a digital caliper before each test (width = 3.5 ± 0.3 mm, thickness = 1.9 ± 0.4 mm). Using WinAGS Lite software, the tensile strength and elongation at break were determined. For each PU formulation a minimum of five samples were tested and the average values for tensile strength and elongation at break are reported. The plots shown for elongation (%) vs. stress (MPa) were created by averaging all PU sample data sets. All original stress-strain data is available in Appendix B.

Water content of bio-based polyols was determined through Karl Fisher titration (Mettler Toledo automatic titrator DL31).

# 4.0 RESULTS AND DISCUSSION

## 4.1 REPLICATION OF ADFAST PRODUCT

The first phase of this project focused on the original polyurethane formula currently produced by Adfast. This polyurethane is the base for many of their commercial sealant products. The reaction was replicated on a small scale at McGill and the product was compared to a sample of Adfast's product from their facility.

The polyurethane reaction was tracked using FTIR, as well as GPC. Samples were taken at various times over the three-hour reaction time. The isocyanate peak located at ~2270 $cm^{-1}$ can been seen in Figure 11. It appears with the addition of the IPDI, and the intensity stabilizes at ~3 hours of reaction as see in Figure 12. The NCO peak intensity correlates with the concentration of NCO groups in the reaction media: as IPDI reacts with PPG, creating urethane linkages from isocyanate groups and hydroxyl groups, the number of NCO groups in the resin is reduced until all of the IPDI has reacted. The stabilization of the NCO peak indicates than the reaction has been completed, and that the NCO content of the resin has reached its equilibrium value. Because the IPDI has a functionality of two, even if it has reacted with PPG using one NCO group, the remaining NCO group will still contribute to the intensity of the FTIR NCO peak. Because Adfast's desired product is only a capping of the PPG with two diisocyanates, the equilibrium NCO content is due to the NCO groups that are on the ends of the polyurethane. The urethane peak located at ~1720 $cm^{-1}$ can also be used to track the reaction. As the isocyanate peak decreases, the urethane peak increases in intensity, confirming the reaction.

The reaction conversion can be calculated using the calculations below where X is conversion, $T_{NCO}$ (%) is the NCO peak transmittance, $A_{NCO}$ is the NCO peak absorbance and $A_{NCO^{\circ}}$ is the NCO peak absorbance at t=0 of the reaction.

$$X(\%) = 1 - \frac{A_{NCO}(\%)}{A_{NCO^{\circ}}(\%)} \times 100\%$$

$$A_{NCO}(\%) = 100 - T_{NCO}(\%)$$

The conversion after 180 minutes is found to be 65% (Figure 12). This is consistent with the desired reaction, as not all isocyanate groups are desired to be converted into urethane linkages.

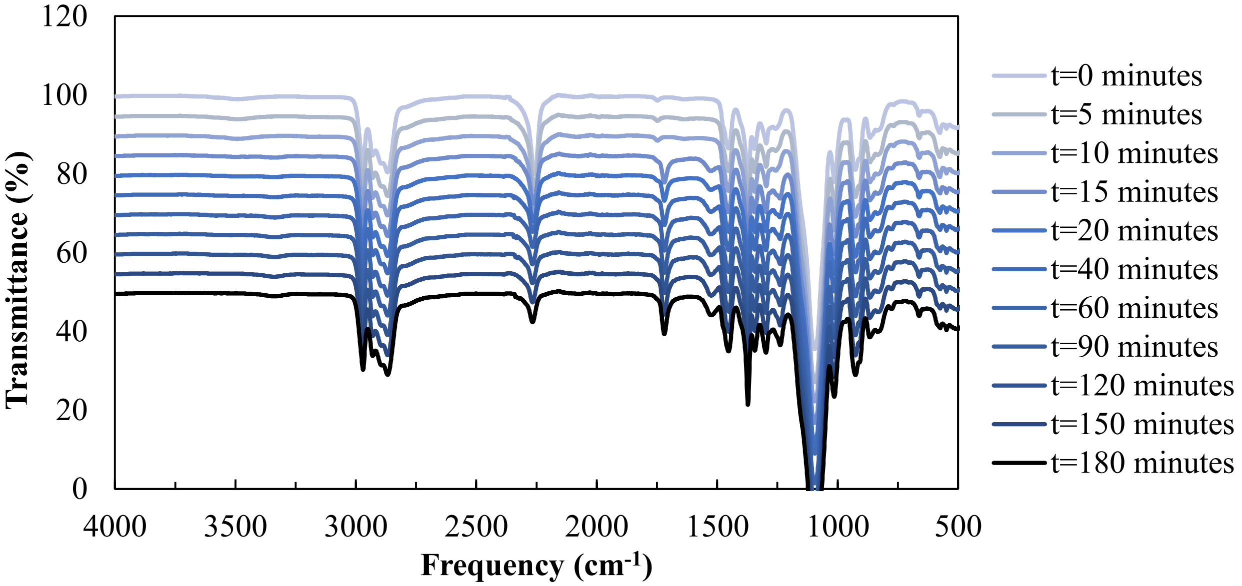


*Figure 11: FTIR spectra of polyurethane reaction for 1.7 mol IPDI/mol PPG reaction. NCO peak located at ~2270 cm$^{-1}$ indicates the presence of NCO groups from free isocyanate. Urethane peak at ~1720 cm$^{-1}$ indicates the formation of urethane bonds.*

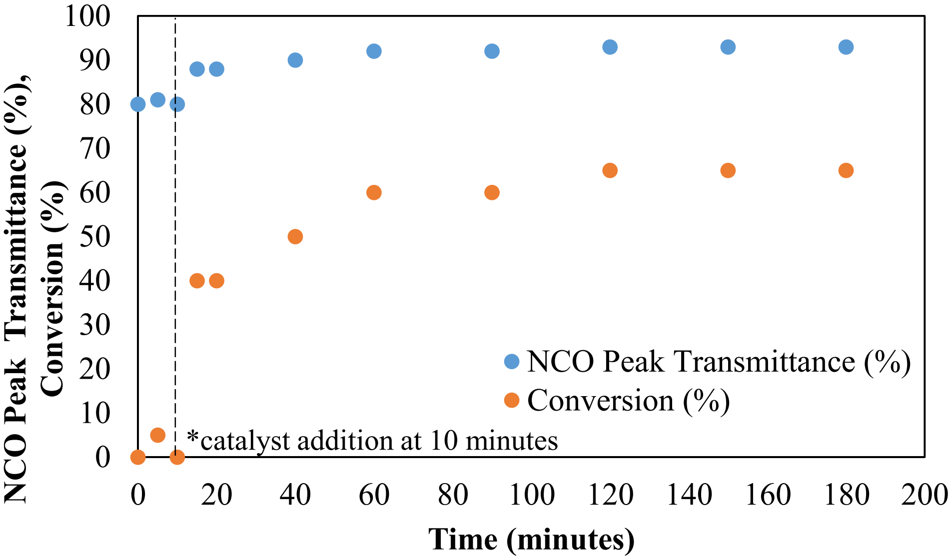


*Figure 12: Intensity of NCO peak (% transmittance) over reaction time and calculated conversion for 1.7 mol IPDI/mol PPG reaction.*

Adfast measures the NCO content of their PU resins before the addition of the end-capper using titrations. Theoretical calculations for calculating NCO content of polyurethanes are shown below.[59] Theoretically, the 1.7 mol IPDI/mol PPG formula results in a free NCO content of 1.4%.

If an equal number of equivalents of PPG and IPDI were added to one another (1.0 mol IPDI/mol PPG, since both reactants have a functionality of 2.0), the resulting resin would have a theoretical free NCO content of 0%.

To calculate the theoretical NCO content, the following equations are used:

$$n = \frac{\left(\frac{42}{y}\right) \times z}{x + y + z}$$

where x = polyol equivalent weight

y = isocyanate equivalent weight

n = desired % NCO of pre-polymer (as fraction)

z = additional grams of isocyanate needed

Using the equation above, the NCO content of Adfast's original 1.7 mol IPDI/mol PPG formulation is calculated:

where x = 2000 g/mol

y = 111 g/mol

Given that 1.7 mol IPDI/mol PPG→ 0.87 mol IPDI/0.5 mol PPG

$$Total\ IPDI = 0.87\ mol\ \times 222 \frac{g}{mol} = 193\ g$$

Therefore:

$$z = 193\ g\ - 111\ g = 82\ g$$

Solving for n, the % NCO gives:

$$n = \frac{\left(\frac{42}{111}\right) \times 82}{2000 + 111 + 82} = 0.01 = 1.4\%\ NCO$$

Samples were also taken before and after the one-hour reaction of the PU with the silane end-capper to verify the end-capping reaction. As the silane end-capper reacts with the free isocyanate in the resin, the NCO groups will no longer be visible in the FTIR spectra. To ensure that all free-NCO in the resin has been end-capped, Adfast uses FTIR. In Figure 13, the NCO peak (~2270 $cm^{-1}$) is seen after 180 minutes of reaction. The peak is eliminated after 1 hour of reaction with the silane end-capper. The urethane peak (~1720 $cm^{-1}$) is seen in both the un-capped and capped resin.

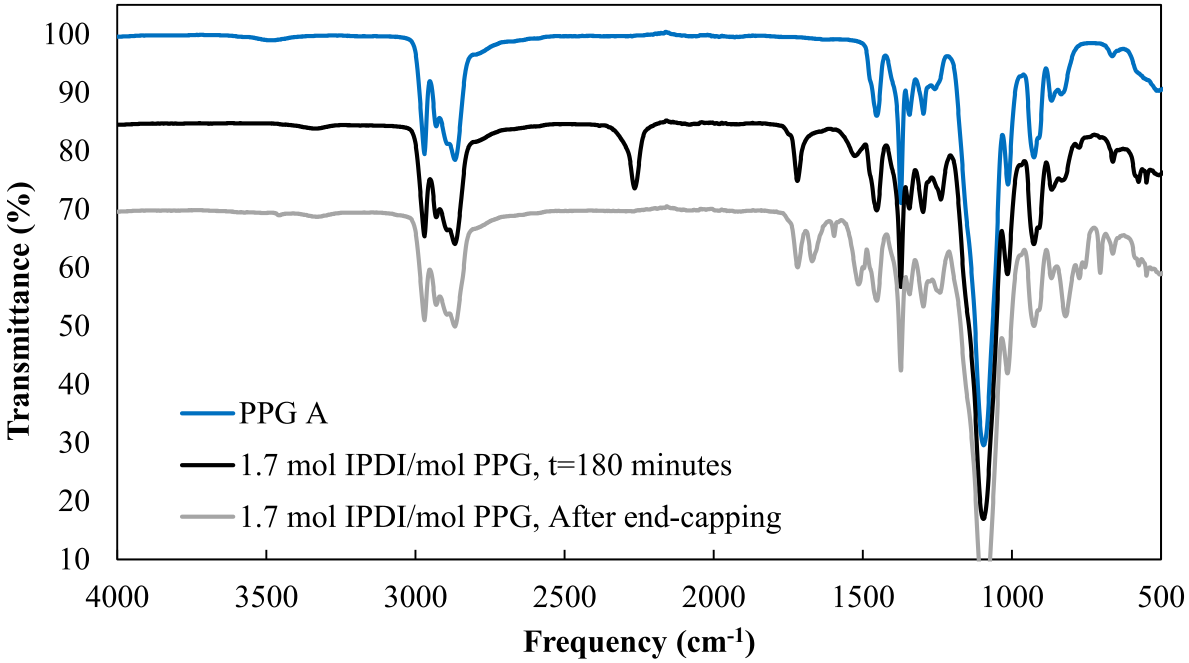


*Figure 13: FTIR spectra of 1.7 mol IPDI/mol PPG PU before and after end-capping. Spectra have been shifted vertically by 15% and 30% in order to compare.*

In order to verify that the final resin produced in the McGill lab was the polyurethane desired, FTIR was used. Figure 14 compares the FTIR spectra for the PPG/IPDI PU resin (after addition of end-capper) produced at McGill with a sample of resin provided by Adfast. It should be noted that in the trial displayed in Figure 14, all free NCO was eliminated in the product by the end-capping reaction. This is confirmed by the lack of any NCO peak (~2270 $cm^{-1}$) in the FTIR spectra.

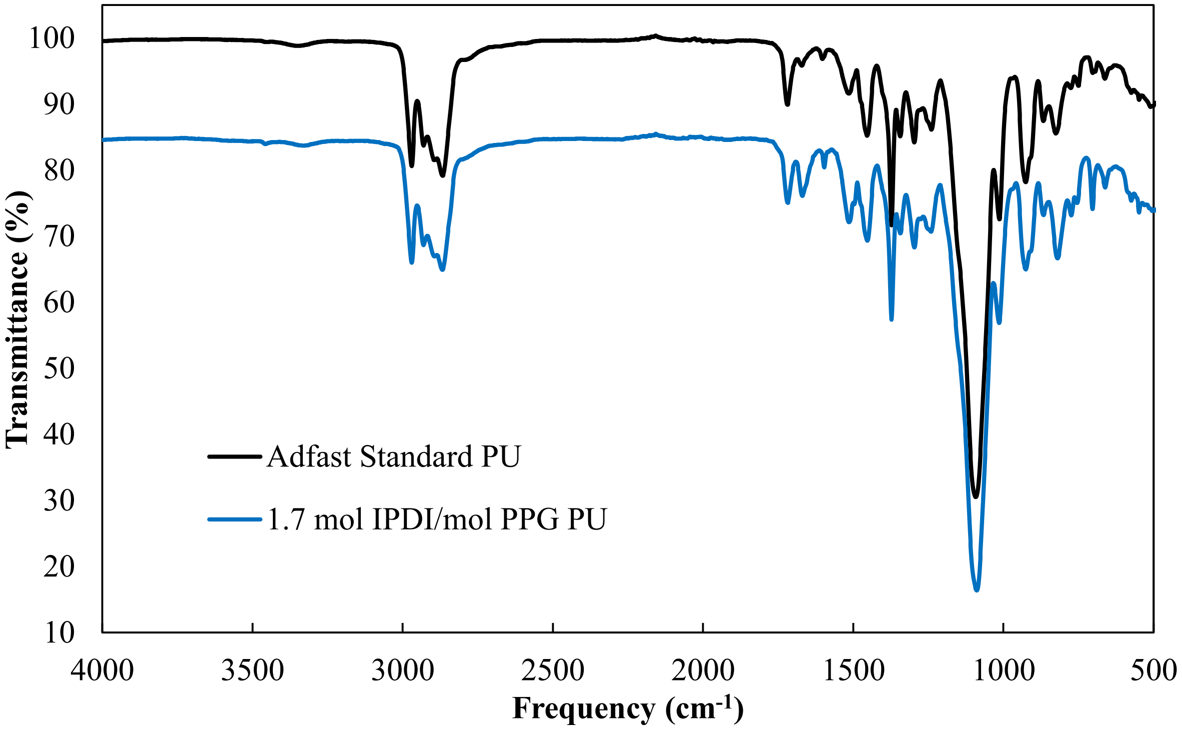


*Figure 14: FTIR spectra of 1.7 mol IPDI/mol PPG sample vs. Adfast standard sample. Spectra have been shifted vertically by 15% transmittance in order to compare.*

When comparing multiple batches of 1.7 mol IPDI/mol PPG PU synthesized at McGill, a variation in the shape of the molecular weight distribution from the GPC traces is seen in Figure 15. This same variation is seen between three batches of Adfast product with the same ratios of reactants (Figure 15). The molecular weights of the resins were estimated based on a PMMA calibration using GPC and are presented in Table 5. The formulations for these resins are presented in Table 6. The molar ratios of IPDI/PPG in each Adfast formulation were calculated to be as follows: 1.76 mol IPDI/mol PPG for LAB-6708, 1.74 for LAB 7064 and 1.73 for LAB 7065. LAB 7065 used an alternate end-capper, N-(n-butyl)-3 aminopropyltrimethoxysilane, but it has a comparative molecular weight and should not affect the molecular weight distribution. Because Adfast is targeting short chains of PPG macro-monomers, the molecular weight distribution and the average molecular weight of the resin is sensitive to varying chain lengths (±1 PPG unit). Based on the varying molecular weight distributions and calculated molecular weights from the GPC traces, it was concluded that variability among formulations was expected and acceptable. From Adfast's perspective, since they were not aware of this variability, it can be concluded that these variations in molecular weight distributions did not greatly affect the final product qualities.

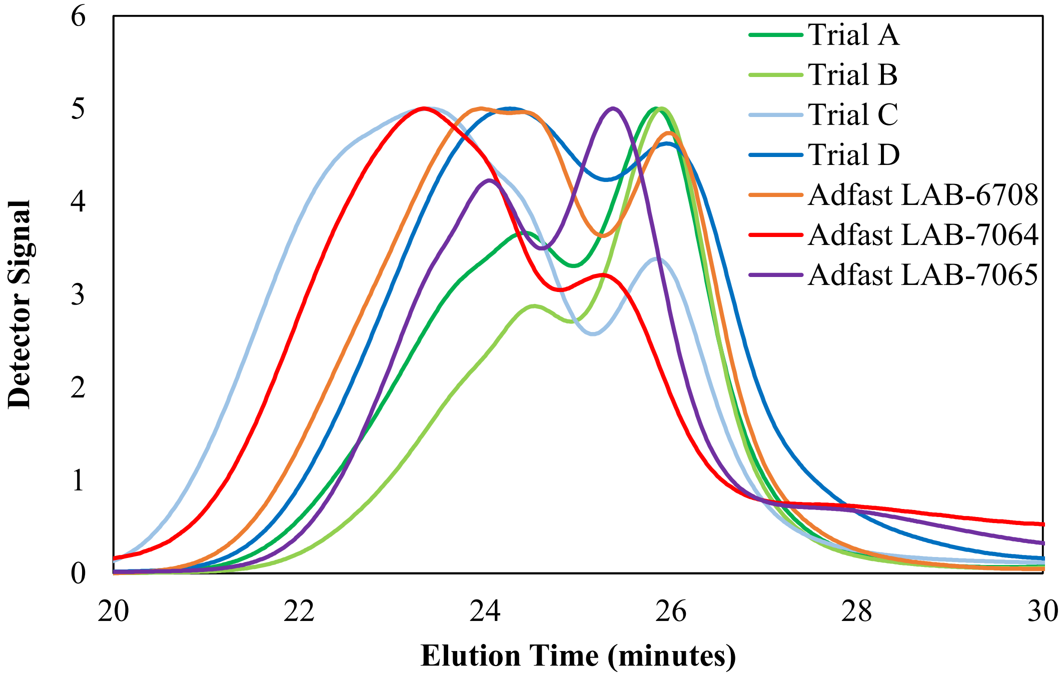


*Figure 15: Comparison of normalized GPC traces of multiple 1.7 mol IPDI/mol PPG trials.*

*Table 5: GPC $M_n$ values for 1.7 mol IPDI/mol PPG trials.*

| Formula | Average $M_n$ (g/mol) | Dispersity (Đ) | Left Peak $M_n$ (g/mol) | Right Peak $M_n$ (g/mol) |
|---|---|---|---|---|
| LAB-6708 | 14,000 | 1.62 | 20,800 | 8,500 |
| LAB-7064 | 20,800 | 1.65 | 29,000 | 11,200 |
| LAB-7065 | 14,300 | 1.36 | 20,400 | 10,500 |
| Trial A | 11,500 | 1.53 | 20,800 | 8,500 |
| Trial B | 10,200 | 1.45 | 15,900 | 8,400 |
| Trial C | 16,800 | 2.18 | 28,000 | 7,800 |
| Trial D | 21,100 | 1.80 | 20,100 | 8,700 |

*Table 6: Formulations for Adfast standard samples in wt%.*

| Adfast Formulation | PPG 4,000 g/mol | Water Scavenger (4-methyl-benzenesul phonylo isocyanate) | IPDI | Fascat® 4202 | Silane End-capper | IPDI/PPG Molar ratio |
|---|---|---|---|---|---|---|
| LAB-6708 | 83.10% | 0.83% | 8.11% | 0.05% | 7.91% (30% excess end-capper*) | 1.76 |
| LAB-7064 | 83.97% | 0.83% | 8.13% | 0.05% | 6.89% (3% excess end-capper*) | 1.74 |
| LAB-7065 | 84.55% | 0.84% | 8.14% | 0.05% | 6.35% (3% excess end-capper**) | 1.73 |

*End-capper: N-phenyl γ-aminopropyltrimethoxysilane
**End-capper: N-(n-butyl)aminopropyltrimethooxysilane

GPC was used to track the molecular weight of the resin as the reaction occurred, as shown in Figure 16. The polyurethane was found to have a bimodal molecular weight distribution. From the integration of the polyurethane GPC curves, shown in Figure 16, the average molecular weight of the leftmost peak is greater than twice the molecular weight of the right peak. This suggests that the bimodal distribution is due to PPG units reacting with two IPDI molecules (the right-most peak) as well as the formation of dimers (polymer chains containing two PPG units) and trimers (chains with three PPG units) which result in the left peak on the GPC traces. The number average molecular weight ($M_n$) is seen to increase linearly throughout the 180 minute reaction time, after the addition of catalyst, as seen in Figure 17. The $M_n$ of the rightmost peak stays fairly constant over time and the $M_n$ of the leftmost peak increases with time. This supports the hypothesis that will be discussed further in the following section: that the left peak is due to polymer chains containing more than one PPG unit.

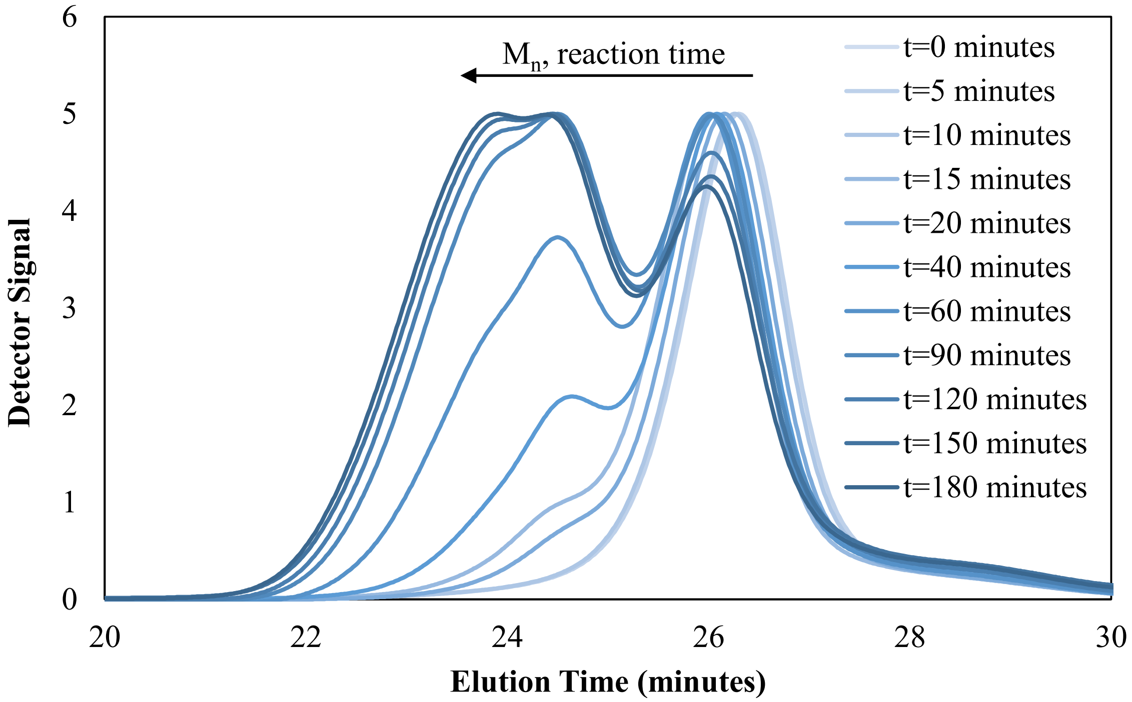


*Figure 16: Normalized GPC traces for 1.7 mol IPDI/mol PPG over 3 hour reaction time.*

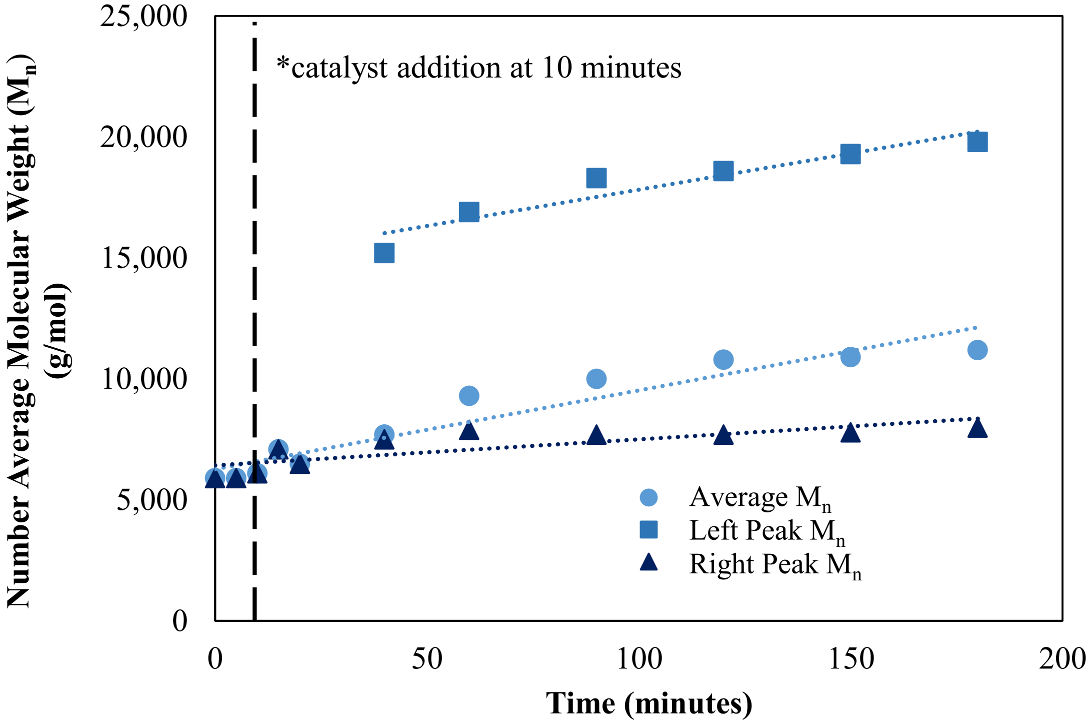


*Figure 17: $M_n$ vs. time for 1.7 mol IPDI/mol PPG reaction.*

## 4.2 OPTIMIZATION OF PPG/IPDI SYSTEM

Based on the results from the 1.7 mol IPDI/mol PPG synthesis and the GPC curves of the other Adfast samples, a series of experiments were conducted to further explore the bimodal molecular weight distribution of the polyurethane. It was hypothesized that by increasing the IPDI concentration in the formulation, the polymer chains in the final PU resin would be shorter (contain chains made up of fewer additional PPG units). Three additional syntheses were performed, each gradually increasing the amount of IPDI that was added. All three experiments with increased IPDI/PPG molar ratios (2.0, 2.5 and 3.0) were found to have narrower molecular weight distributions and lower molecular weights as seen in Figure 18. One more experiment was performed, this time decreasing the amount of IPDI added, and the molecular weight was found to increase greatly. In the 1.4 mol IPDI/mol PPG experiment the viscosity was qualitatively seen to have a higher viscosity than the other formulas.

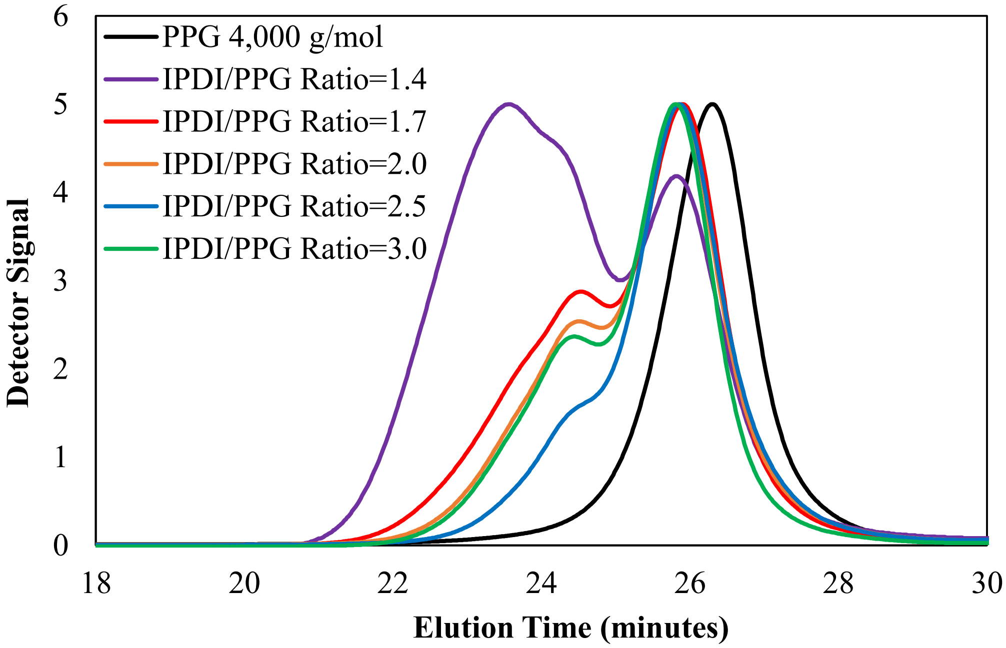


*Figure 18: Normalized GPC traces for IPDI/PPG ratio experiments.*

GPC was used to estimate the molecular weights of the PU resins, as well as to estimate the molecular weights of each of the two peaks in the distributions (Table 7). GPC was also used to find the comparable molecular weights of the PPG 4,000 g/mol, IPDI, and silane end-capper (Table 8). Based on these molecular weights, the compositions of the PU resins were estimated. A graphical explanation is offered in Figure 19 for the calculation of molecular weights for varying polyurethane chain lengths. By comparing the $M_n$ values from the GPC for each of the resins, to the theoretical resin $M_n$ values (based on differing chain lengths) listed in Table 9, the composition of each peak for each PU resin can be estimated. Based on this method, the right-most peak of the PU resins is believed to be chains containing only one PPG unit ($M_n \approx 8{,}700$ g/mol). The left peaks for each of the resins are believed to be chains with multiple PPG units. The left peaks in the 3.0, 2.5, 2.0 and 1.7 mol IPD/mol PPG samples ($15{,}600 < M_n < 22{,}500$), are suspected to be chains made up of 2-3 PPG units. The large left peak in the 1.4 mol IPDI/mol PPG sample is expected to contain longer chains up to 5 PPG units ($M_n \approx 36{,}300$ g/mol) to have a $M_n$ of 33,500 g/mol).

*Table 7: $M_n$ values for IPDI/PPG ratio experiments.*

| Formula | Average $M_n$ (g/mol) | Dispersity (Đ) | Left Peak $M_n$ (g/mol) | Right Peak $M_n$ (g/mol) |
|---|---|---|---|---|
| 1.4 mol IPDI/mol PPG | 14,300 | 1.63 | 33,500 | 7,900 |
| 1.7 mol IPDI/mol PPG | 10,200 | 1.45 | 15,900 | 8,400 |
| 2.0 mol IPDI/mol PPG | 9,700 | 1.34 | 18,000 | 8,400 |
| 2.5 mol IPDI/mol PPG | 8,600 | 1.24 | 18,200 | 8,400 |
| 3.0 mol IPDI/mol PPG | 9,400 | 1.31 | 18,700 | 8,700 |

*Table 8: Theoretical $M_n$ values vs. GPC $M_n$ for raw materials.*

| Component | Symbol used in Figure 19 | Theoretical $M_n$ (g/mol) | GPC $M_n$ Based on PMMA Standard (g/mol) |
|---|---|---|---|
| PPG 4,000 g/mol | ▬ | 4,000 | 6,300 |
| IPDI | ● | 222 | 600 |
| Silane End-capper | ⬟ | 226 | 600 |

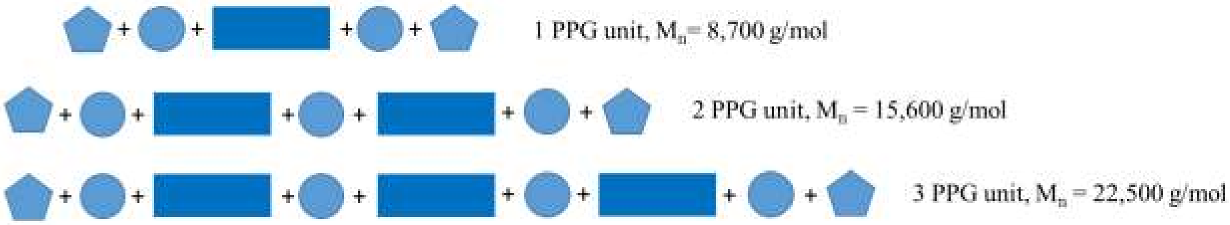


*Figure 19: Determination of number of PPG units in molecular weight distribution.*

*Table 9: Theoretical $M_n$ values for polyurethanes with varying number of PPG units.*

| # of PPG Units | # of IPDI Units | # of End-capper Units | Theoretical $M_n$ (g/mol) |
|---|---|---|---|
| 1 | 2 | 2 | 8,700 |
| 2 | 3 | 2 | 15,600 |
| 3 | 4 | 2 | 22,500 |
| 4 | 5 | 2 | 29,300 |
| 5 | 6 | 2 | 36,300 |

This analysis provided new information to Adfast about the composition of their polymers. It proved that the resin molecular weight distribution could be tailored by adjusting the molar ratio of IPDI/PPG. For this project, a narrower distribution was deemed unnecessary for Adfast's products as the current standard product has a broad, bimodal distribution, resulting in the properties that Adfast desired in their sealants. Achieving a narrower distribution would also come at the extra cost of increased IPDI in the formulation. Based on the bimodal and varying distributions of Adfast's current products, it was concluded that a narrow distribution was not a critical parameter when developing bio-based polyurethanes, therefore a starting point of 1.7 mol IPDI/mol bio-based polyol would be used in this project.

## 4.3 CHARACTERIZATION OF BIO-BASED POLYOLS

Three commercial bio-based polyols were ordered to assess their potential as replacements to the PPG diol currently used to produce Adfast's polyurethanes. From Sovermol®, a subsidiary of BASF, the polyols Sovermol® 830 and Sovermol® 908 were ordered. A sample of the experimental polyol Myrinol™ DG-110 was also ordered from GC Innovation America. A summary of the properties provided from the suppliers for each of these three bio-based polyols is presented below in Table 10.

*Table 10: Summary of key properties for bio-based polyols.*

| Polyol | Functionality | OH # (mg KOH/g) | Description |
|---|---|---|---|
| Sovermol® 830 (see Appendix A) | 2.6 | 241 | Branched oleochemical polyether/polyester |
| Sovermol® 908[41] | 2.0 | 206 | Aliphatic dimer alcohol |
| Myrinol™ DG-110[42] | 2.0 | 113 | Linear polyester polyol, derived from bio-succinic acid and diethylene glycol. |

For Myrinol™ DG-110, the MSDS identified the polyol as poly(diethylene glycol succinate) (Figure 20) and $^1$H-NMR was used to verify the structure. Figure 21 shows the $^1$H-NMR spectra of Myrinol™ DG-110 and identifies the protons that correspond to those identified on the chemical structure in Figure 20.

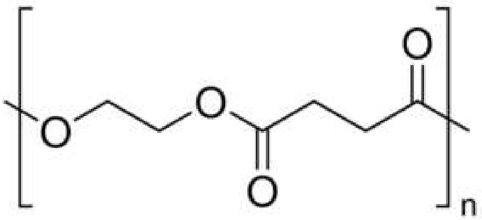


*Figure 20: Chemical structure of Myrinol™ DG-110 polyol (poly(diethylene glycol succinate)).*

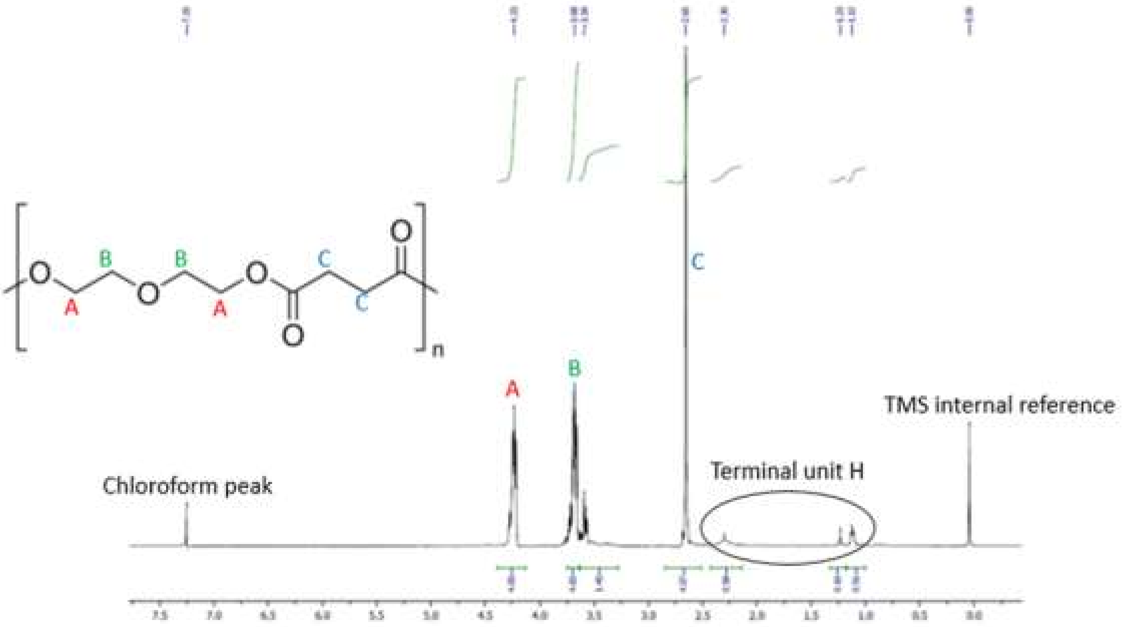


*Figure 21: $^1$H NMR spectra for Myrinol™ DG-110 polyol (poly(diethylene glycol succinate)).*

Sovermol® did not provide the structures of their polyols: Sovermol® 830 and Sovermol® 908. Using $^1$H-NMR (Figure 23) and the information provided by the supplier, the structure of the Sovermol® 908 polyol was hypothesized to be that shown in Figure 22. Sovermol® produces their polyols from epoxidation of natural oils such as rapeseed oil, castor oil, soybean oil and palm kernel oil.[14, 41]

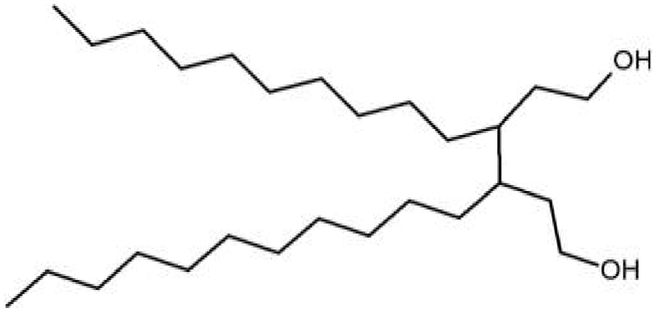


*Figure 22: Hypothesized chemical structure of Sovermol® 908 polyol.*

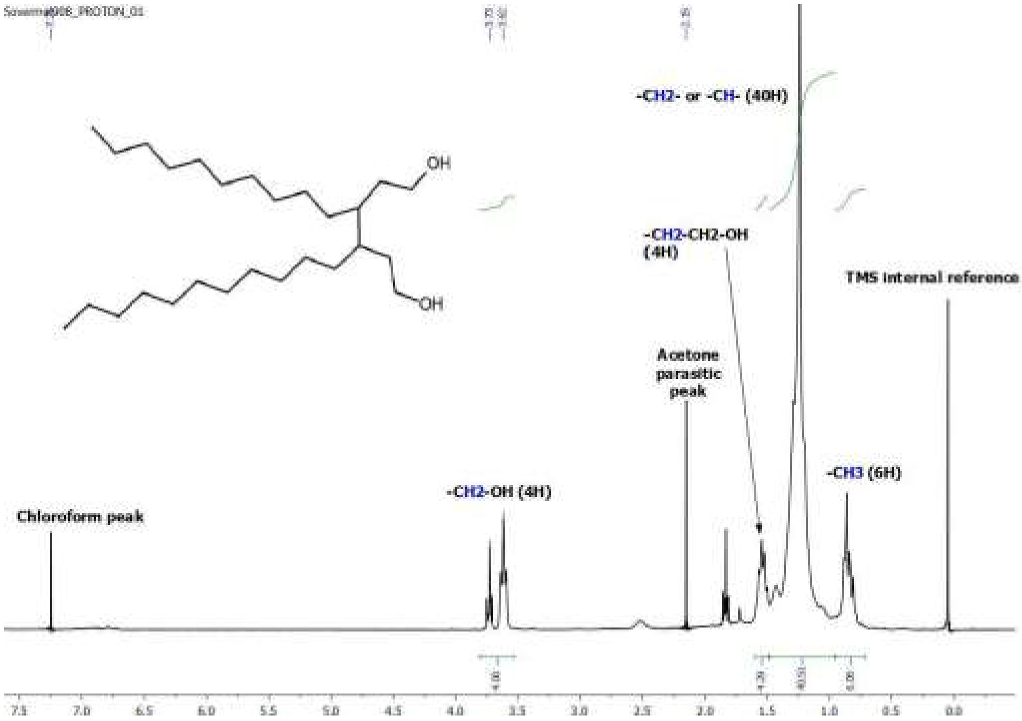


*Figure 23: $^{1}$H-NMR spectra for Sovermol® 908 polyol.*

The Sovermol® 830 polyol has an average functionality of 2.6, meaning it is likely a mixture of polyols with different functionalities. Because of this, the structure was not able to be determined conclusively. For the purpose of this thesis, the bulk material was assumed to have the particular functionality and OH# as stated by the supplier (Table 10). Formulations for using the Sovermol® 830 were still derived without knowing the explicit structure and composition of the polyol. From the supplier it is known that the Sovermol® 830 polyol is a "branched oleochemical polyether/polyester".

Samples of the bio-based polyols were sent to the Adfast lab where they were tested for water content using Karl Fischer titration. This was valuable information as the water content of the polyol determines how much water scavenger should be added to the polyol before the addition of the diisocyanate. The results from these tests are displayed in Table 11.

*Table 11: Water content of PPG vs. bio-based polyols (from Adfast labs).*

| Polyol | Water Content |
|---|---|
| PPG 4,000 g/mol | 0.5% |
| Sovermol® 830 | 0.04% |
| Sovermol® 908 | 0.05% |
| Myrinol™ DG-110 | 0.03% |

The water content testing showed that all three bio-based polyols had very low water content—therefore less water scavenger could be added during the synthesis. The amount of scavenger to be added was calculated based on keeping the molar ratio of scavenger/water the same as the original Adfast formulation.

GPC was used to compare the molecular weights of the three bio-based polyols to the original 4,000 g/mol PPG diol (Figure 24). The two Sovermol® polyols were found to have narrow molecular weight distributions (Đ = 1.04 for Sovermol® 830 and Đ = 1.05 for Sovermol® 908), similar to the PPG polyol (Đ = 1.11). The Myrinol™ polyol was found to have a broader molecular weight distribution (Đ = 1.74), likely due to the Myrinol™ polyol being synthesized by the step-growth polymerization of succinic acid and diethylene glycol. Products of step-growth polymerizations have a theoretical Đ = 2.0 at large reaction extents, explaining the higher dispersity of the Myrinol™ DG-110 polyol.[60]

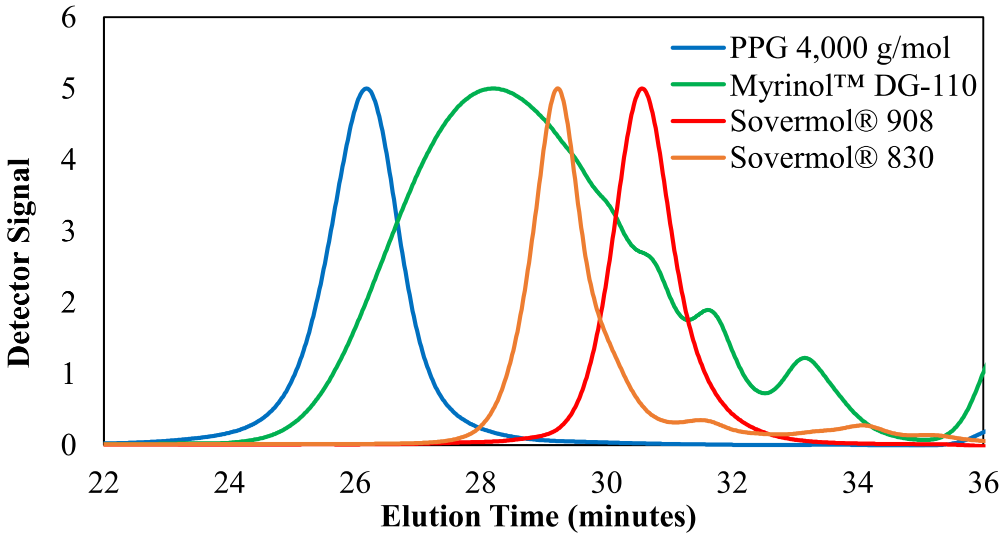


*Figure 24: Normalized GPC traces for PPG 4,000 g/mol and bio-based polyols.*

In order to calculate the amount of IPDI to be added to each bio-based polyol, the molecular weights of the three bio-based polyols had to be calculated. From the suppliers, the hydroxyl number (OH #) and functionality were given for each polyol (Table 10). Using the equations below, the molecular weights were calculated.[61] Sample calculations are shown for determining the molecular weight of the Myrinol™ DG-110 polyol.

$$Equivalent\ Weight\ \left(\frac{g}{mol}\right) = \frac{56.1\ \times 1000}{OH\ \#}$$

$$Molecular\ Weight\ \left(\frac{g}{mol}\right) = Equivalent\ Weight\ (\frac{g}{mol}) \times Functionality$$

For Myrinol™ DG-110 polyol: OH# = 113, Functionality = 2.0

$$Equivalent\ Weight\ \left(\frac{g}{mol}\right) = \frac{56.1\ \times 1000}{113} = 497\frac{g}{mol}$$

$$Molecular\ Weight\ \left(\frac{g}{mol}\right) = \ 497\ \left(\frac{g}{mol}\right) \times 2.0 = 993\frac{g}{mol}$$

When the GPC molecular weight distributions are integrated to determine the molecular weights, a PMMA calibration is used, meaning that the molecular weights can be used for comparison and for estimation of composition of resins, but they are not the true values and should not be compared to the theoretical molecular weight values calculated using the polyol OH# and functionality. The GPC molecular weights, dispersities and theoretical molecular weights for the polyols used in this project are displayed below in Table 12.

*Table 12: GPC $M_n$ values vs. theoretical molecular weights for polyols.*

| Polyol | GPC Molecular Weight ($M_n$) based on PMMA calibration (g/mol) | GPC Dispersity (Đ) | Theoretical Molecular Weight (g/mol) |
|---|---|---|---|
| PPG 4,000 g/mol | 6,300 | 1.11 | 4,000 |
| Sovermol® 830 | 1,800 | 1.04 | 605 |
| Sovermol® 908 | 1,100 | 1.05 | 545 |
| Myrinol™ DG-110 | 1,400 | 1.74 | 993 |

The viscosities of the bio-based polyols were compared to the viscosity of the 4,000 g/mol PPG polyol at room temperature (Figure 25). It was found that the Sovermol® polyols had viscosities similar to PPG, but the Myrinol™ DG-110 polyol had a higher viscosity. This is likely due to the Myrinol™ DG-110 polyol being a polyester which is not as flexible as the polyether PPG.

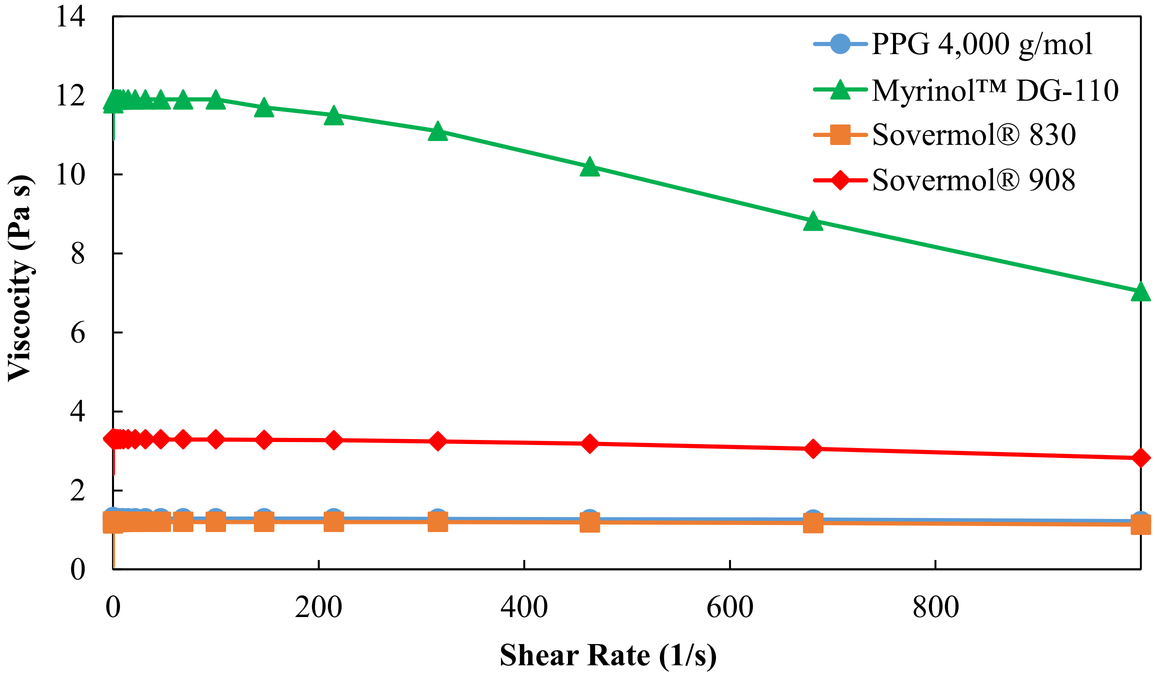


*Figure 25: Viscosities of bio-based polyols vs. PPG.*

## 4.4 CHARACTERIZATION OF BIO-BASED ISOCYANATES

The final stage in this project was to create a fully bio-based PU resin, using both a bio-based polyol and a bio-based diisocyanate. Ethyl ester L-lysine diisocyanate (LDI) was selected as a suitable bio-based isocyanate based on its structure (see Figure 26) and commercial availability. LDI is derived from the amino acid L-lysine. Because of its linear structure, it was hypothesized that it would result in a more elastic and less viscous PU than IPDI. LDI has been used to synthesize polyurethanes with poly(lactic acid), poly(ethylene glycol) and poly(ε-caprolactone) because of its non-toxic degradation products. [46, 47]

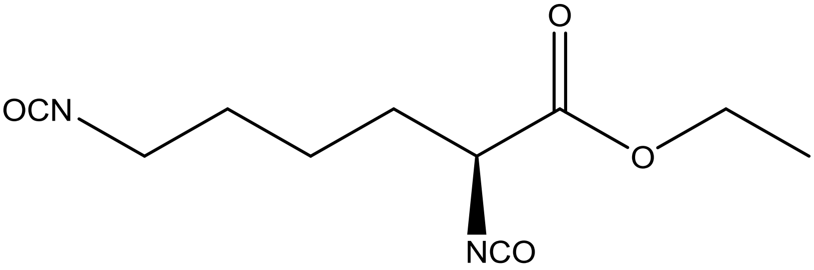


*Figure 26: Structure of ethyl ester L-lysine diisocyanate (LDI).*

## 4.5 CHARACTERIZATION OF PU RESINS

The initial formulations for the polyurethanes using bio-based polyols (Table 4) were derived from keeping the same molar ratio of 1.7 mol IPDI/mol polyol as the original Adfast formula had used. The bio-based polyurethanes were synthesized (using the procedure outlined in Table 2) and characterized in order to compare them to the original Adfast PPG polyurethane. GPC was used to assess the molecular weight distributions and track the reaction. The viscosity and stress-strain properties were tested for all bio-based polyurethanes in order to compare them to the original IPDI/PPG resin.

### 4.5.1 MOLECULAR WEIGHT

Figure 27 shows the normalized GPC traces for the original PPG PU resin in comparison to the bio-based PU resins using IPDI. While the Sovermol® 830 and Sovermol® 908 polyols produced PU resins with molecular weight distributions similar to that of Adfast original IPDI/PPG formula, these resins were found to be very viscous, and very hard once cured. Based on these physical properties they were deemed to be unsuitable for the sealant application. These physical properties will be discussed in length in following sections of this thesis. More in-depth analysis was conducted on the IPDI/Myrinol™ DG-110 PU resin as its lower viscosity and high elongation were more suitable for incorporation into Adfast's sealant products.

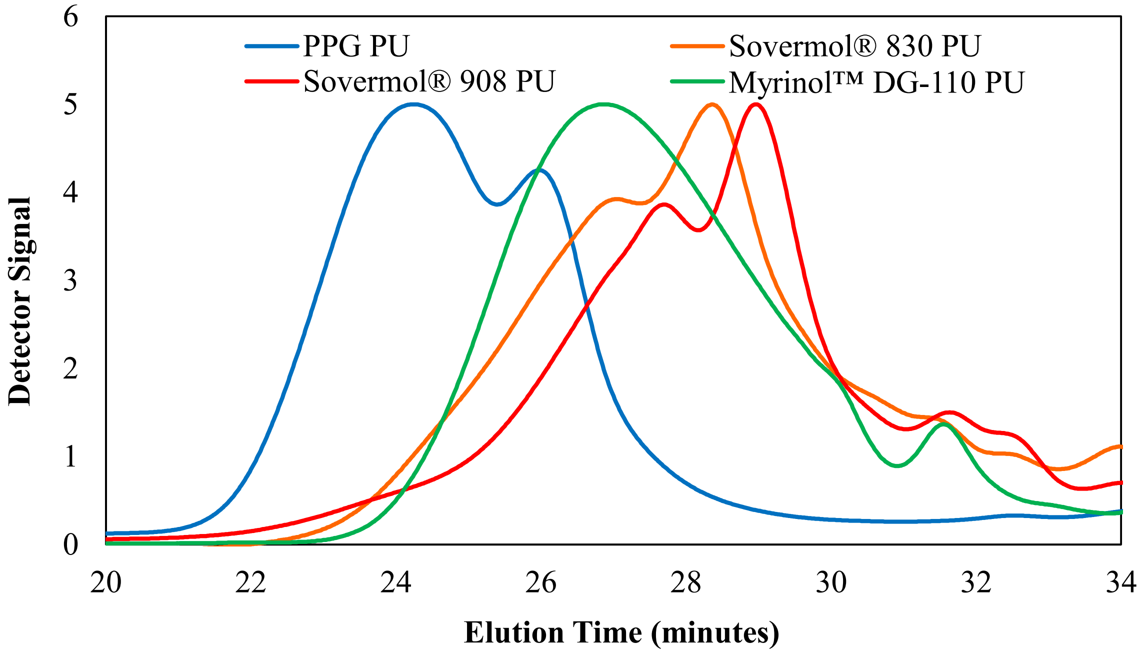


*Figure 27:Normalized GPC traces for bio-based PUs compared to 1.7 mol IPDI/mol PPG PU.*

Similar to the original IPDI/PPG formulation, using the molecular weights of the raw materials, the composition of the bio-based PUs was estimated. For the IPDI/Sovermol® polyols, two trials were performed using each polyol (Figure 28, Figure 29). From the integration of the normalized GPC traces, the average $M_n$ values as well as the $M_n$ values for each of the peaks were estimated and presented in Table 13. From these $M_n$ values and the bimodal molecular weight distribution, the composition of the Sovermol® PU resins was determined to be similar to the IPDI/PPG PU resins. The rightmost peak is believed to be composed of polymer chains with one Sovermol®

polyol unit and the left peak is made of chains of 2-3 polyol units. In the case of Sovermol® 830 PU Trial A (Figure 28), there is a high molecular weight shoulder on the left peak resulting in a high average $M_n$.

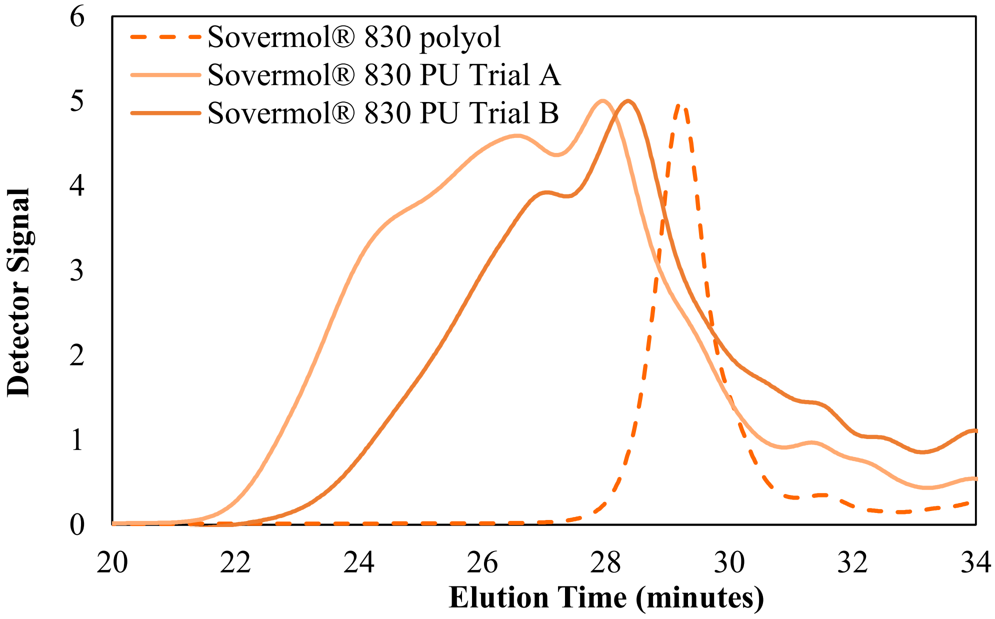


*Figure 28: Normalized GPC traces for Sovermol® 830 PUs.*

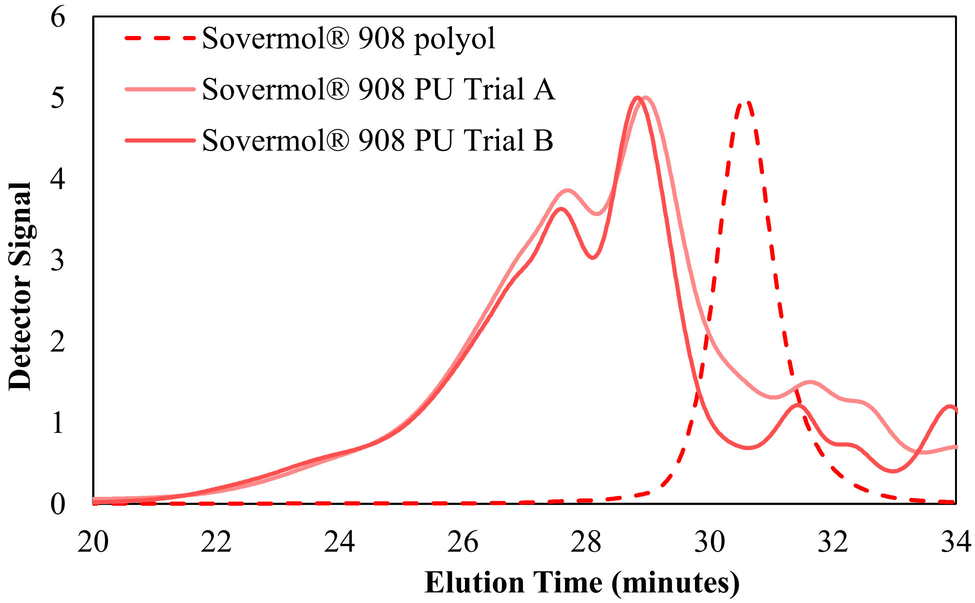


*Figure 29: Normalized GPC traces for Sovermol® 908 PUs.*

*Table 13: GPC $M_n$ values for Sovermol® 830 and Sovermol® 908 PU resins.*

| Formula | Trial | Average $M_n$ (g/mol) | Dispersity (Đ) | Left Peak $M_n$ (g/mol) | Right Peak $M_n$ (g/mol) |
|---|---|---|---|---|---|
| 1.7 mol IPDI/mol Sovermol® 830 | A | 10,800 | 2.06 | 6,900 | 3,200 |
| | B | 5,700 | 1.52 | 5,500 | 2,800 |
| 1.7 mol IPDI/mol Sovermol® 908 | A | 3,700 | 1.35 | 4,300 | 1,700 |
| | B | 3,100 | 1.22 | 3,700 | 2,000 |

When the normalized GPC traces from the reaction of 1.7 mol IPDI/mol Myrinol™ DG-110 are plotted (Figure 30), this reaction does not produce a bimodal distribution as the PPG and Sovermol®-containing PU resins did. This is due to the broad distribution of the Myrinol™ DG-110, and instead of a bimodal distribution, a steady shift in the molecular weight distribution (traces shift left as $M_n$ increases) is seen. The GPC traces were integrated to estimate the sample molecular weights (Table 14), and these were used to determine the compositions. Based on the GPC $M_n$ of the resin in Trial A (5,400 g/mol) and the GPC $M_n$ of the Myrinol™ DG-110 polyol (1,400 g/mol) the resin is suspected to be composed of chains of 1-2 polyols units. In Trial B, the resin $M_n$ was higher (9,800 g/mol), suggesting that it is composed of longer chains with up to 4 polyol units per polymer. Both of these trials used the same ratio of 1.7 mol IPDI/mol Myrinol™ DG-110. Compared to the variation in molecular weight distribution of the 1.7 mol IPDI/mol PPG resins (discussed in Section 4.1), this variation in composition is not unexpected. As seen for all of the PU systems, some variation in molecular weight is expected—likely due to the small scale of the reaction where control of the stoichiometric ratios is more difficult.

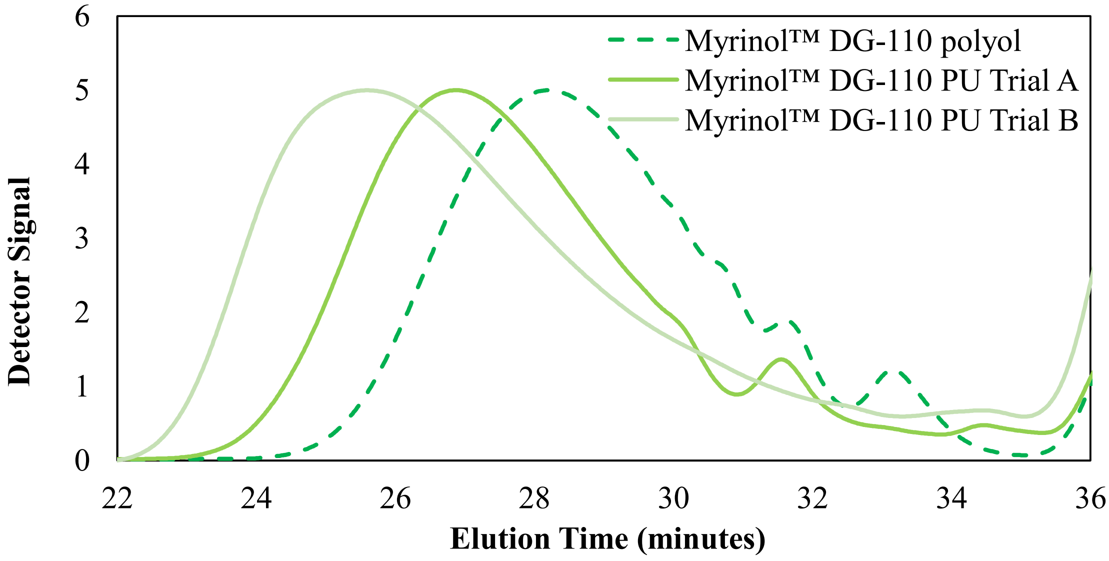


*Figure 30: Normalized GPC traces for Myrinol™ DG-110.*

*Table 14: GPC $M_n$ and Đ values for Myrinol™ DG-110 PU resins.*

| Formula | Trial | Average $M_n$ (g/mol) | Dispersity (Đ) |
|---|---|---|---|
| 1.7 mol IPDI/mol Myrinol™ DG-110 | A | 5,400 | 1.78 |
| | B | 9,800 | 2.34 |

When the normalized GPC traces for the reaction of 1.7 mol IPDI/mol Myrinol™ DG-110 over the reaction time are plotted, the shift in molecular weight (molecular weight increasing as the distribution shifts to the left) is seen. In Figure 31, the peak due to the IPDI is also seen at ~35 minutes elution time. As the reaction progresses, the height of the IPDI peak decreases, verifying that the IPDI is being consumed by the polyurethane reaction. By integrating the GPC traces shown in Figure 31, the composition of the resin can be estimated. After 180 minutes of reaction time, the polymer resin ($M_n$ = 3,100 g/mol) is suspected to be composed of 1-2 units of polyol (polyol $M_n$ = 1,400 g/mol). When the 1.7 mol IPDI/mol Myrinol™ DG-110 average resin $M_n$ is plotted over time, the molecular weight is seen to increase linearly, but more slowly than the IPDI/PPG formulation—the slower increase in $M_n$ being due to the Myrinol™ DG-110 polyol having a lower $M_n$ than the PPG diol (1,400 g/mol vs. 6,300 g/mol) (Figure 32). Both reactions have an $M_n$ at t=0 approximately equal to the $M_n$ of the monomer (Myrinol™ DG-110: 1,400 g/mol, PPG: 6,300 g/mol).

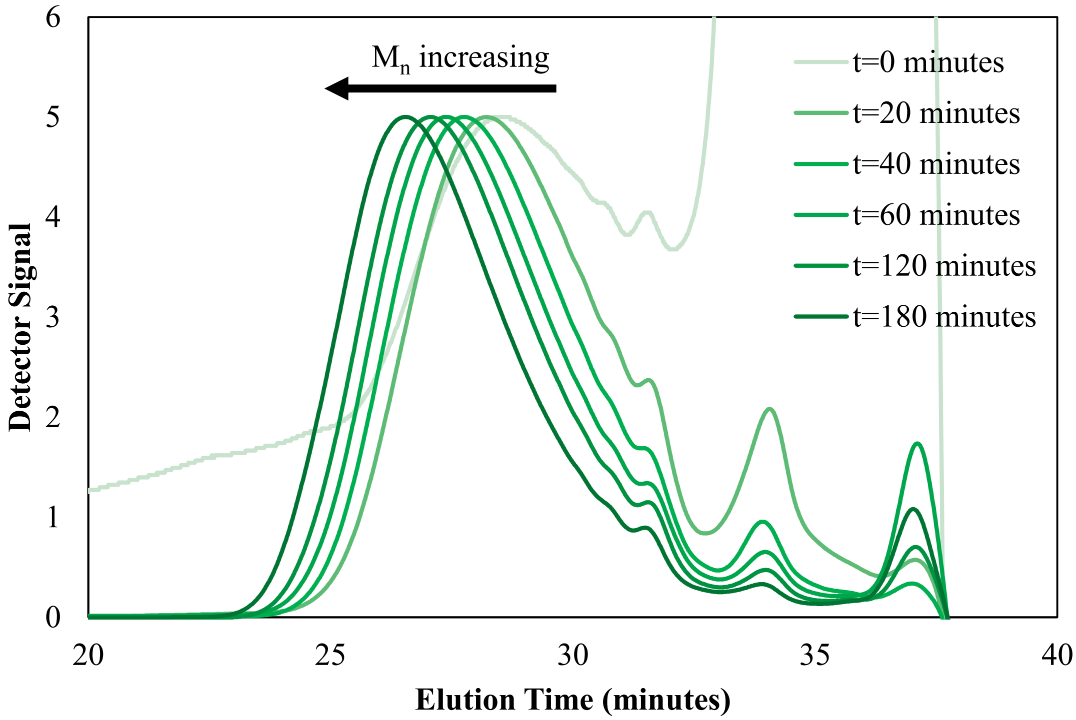


*Figure 31: Normalized GPC traces for 1.7 mol IPDI/mol Myrinol™ DG-110 PU reaction over time.*

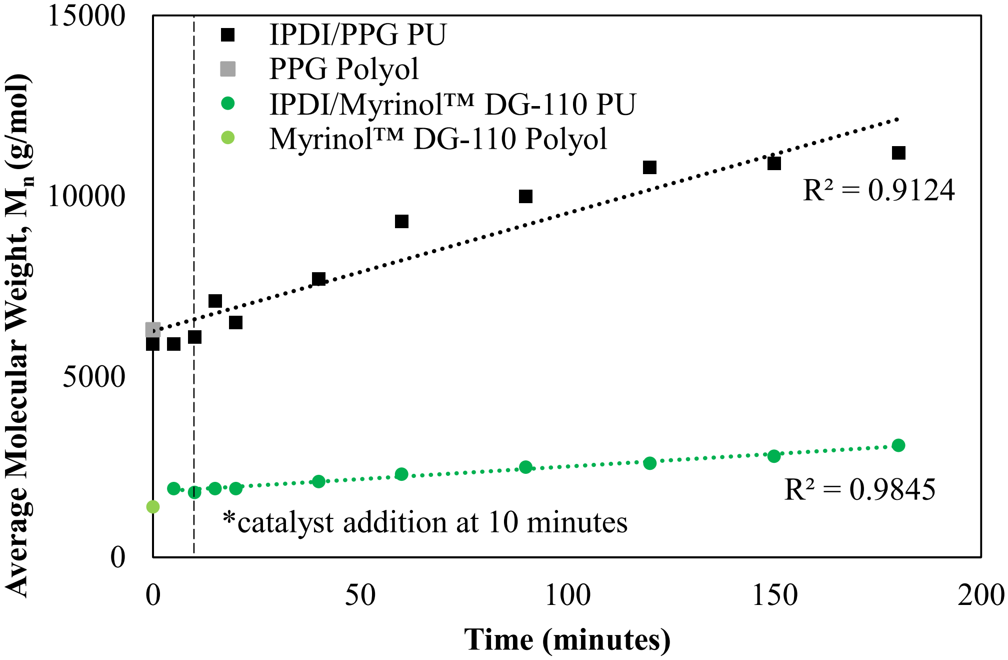


*Figure 32: $M_n$ (measured by GPC via PMMA calibration) vs. reaction time for 1.7 mol IPDI/mol Myrinol™ DG-110 and 1.7 mol IPDI/mol PPG PU.*

It was hypothesized that the Myrinol™ DG-110 polyol may have a higher reactivity than the 4,000 g/mol PPG, because of its primary hydroxyl groups. In general, the reactivity of a polyol increases as the primary hydroxyl content increases.[62] A synthesis was attempted without the use of any catalyst. Unfortunately, from the normalized GPC traces shown in Figure 33, very little polymerization occurred without the use of catalyst.

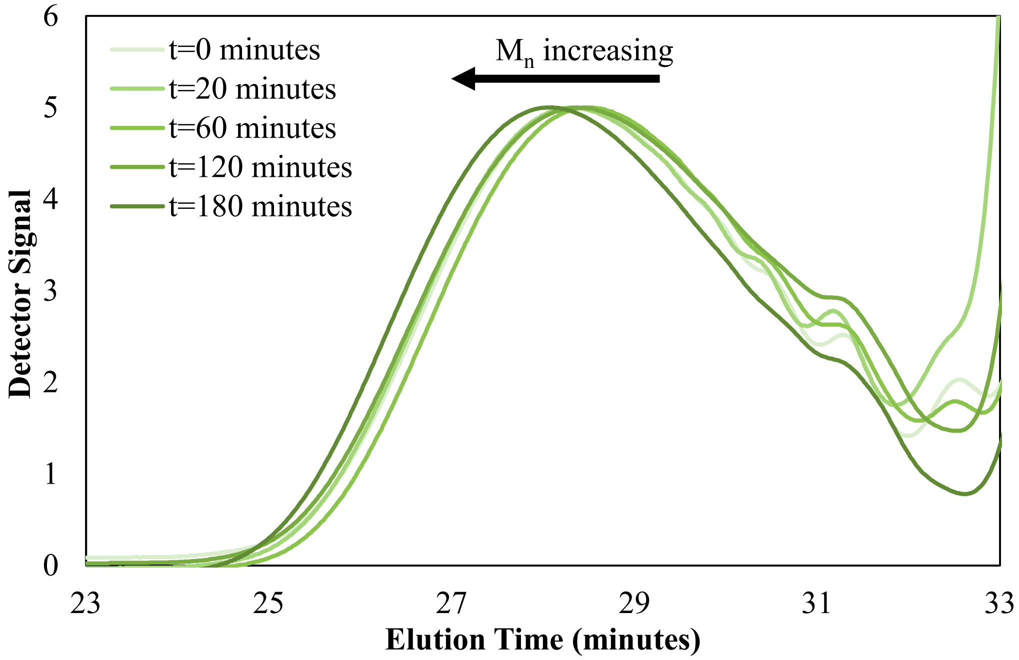


*Figure 33: Normalized GPC traces for Myrinol™ DG-110 PU reaction without use of catalyst.*

### 4.5.2 PHYSICAL PROPERTIES

Using the parallel plate configuration on the rheometer, the viscosity of a sample of end-capped 1.7 mol IPDI/mol PPG PU (after 1 hr reaction with silane end-capper) was measured. Compared to the viscosity of the 4,000 g/mol PPG polyol, the viscosity increased by a factor of 10 with the polyurethane reaction (Figure 34).

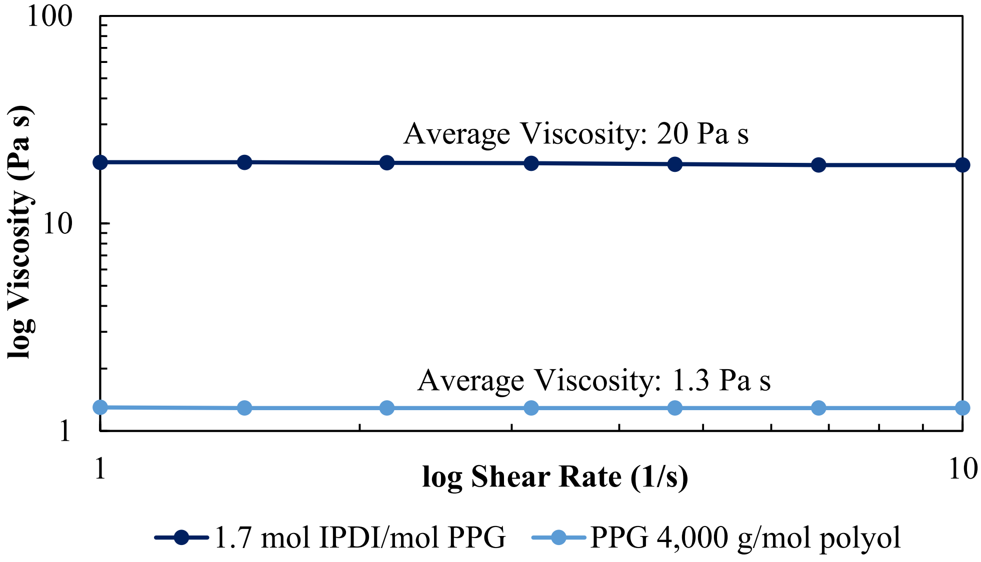


*Figure 34: Viscosity of 1.7 mol IPDI/mol PPG PU vs PPG 4,000 g/mol polyol.*

The bio-based polyol PU resins were measured using the same parallel plate configuration on the rheometer. Immediately following the completion of the end-capping reaction (1 hr reaction of the base PU resin with silane) a sample of resin was removed from the reactor and the viscosity was measured using the rheometer. The viscosities of the bio-based PUs were significantly higher than that of the PPG PU resin. This was expected, as the viscosities of the bio-based polyols (Figure 25) were already higher than the viscosity of the 4,000 g/mol PPG.

Additional experiments were conducted to investigate if the high viscosities of the bio-based resins could be due to the resins beginning to cure immediately after being removed from the reactor. The viscosities of each of the bio-based PUs were measured without the addition of the silane end-capper in order to ensure that no curing would be affecting the viscosity measurement. These values are compared to the viscosities of the end-capped bio-based PU resins in Table 15. The viscosities were still found to be very high (1,200-5,800 Pa s), but >50% lower than the end-capped resin viscosities (4,200-17,700 Pa s). From this data it was concluded that it was unlikely that there was premature curing taking place, and that the difference in un-capped and capped viscosities was only due to the extra length of the molecules after addition of the silane end-capper

*Table 15: Viscosities of un-capped PU resins vs. capped PU resins.*

| Formula | Un-capped Viscosity (Pa s) | Capped Viscosity (Pa s, 20 °C) |
|---|---|---|
| 1.7 mol IPDI/mol PPG | N/A | 24 |
| 1.7 mol IPDI/mol Sovermol® 830 | 5,800 | 17,700 |
| 1.7 mol IPDI/mol Sovermol® 908 | 5,600 | 14,800 |
| 1.7 mol IPDI/mol Myrinol™ DG-110 | 1,200 | 4,200 |

The curing rate for only the 1.7 mol IPDI/mol PPG PU was assessed. For this test, 2 wt% of Reaxis® C417VM catalyst was used to increase the curing rate so that changes in the properties of the resin would be visible over a relatively short period of time. In Figure 35, it is seen that both the loss modulus (G") and the storage modulus (G') of the resin increase over time—an indication of curing. The time at which the two curves cross is referred to as the gel time[63]. While this experiment was interesting, to see the PU curing over time, since it is not a standardized test it was not repeated for the other PU formulations. This test must be standardized by using controlled conditions in order to be able to compare different PU resins. From conversations with Adfast, a more carefully constructed (i.e. smaller plate diameter) parallel plate geometry may also be necessary to get an accurate estimate of curing time. Because the resin relies on the reaction with atmospheric moisture in order to cure, the area of the resin that is against the plate has no access to moisture, therefore the area of sample in contact with the plate should be reduced as much as possible. The curing rate is a key variable for PU formulations as different products will require different curing time ranges. Adfast has products marketed for short curing times and long curing times. The curing rate in general is manipulated by the amount of curing catalyst added to the resin, however it is important to understand how the bio-based resins react with the curing catalyst in order to determine what kind of products they would be appropriate for.

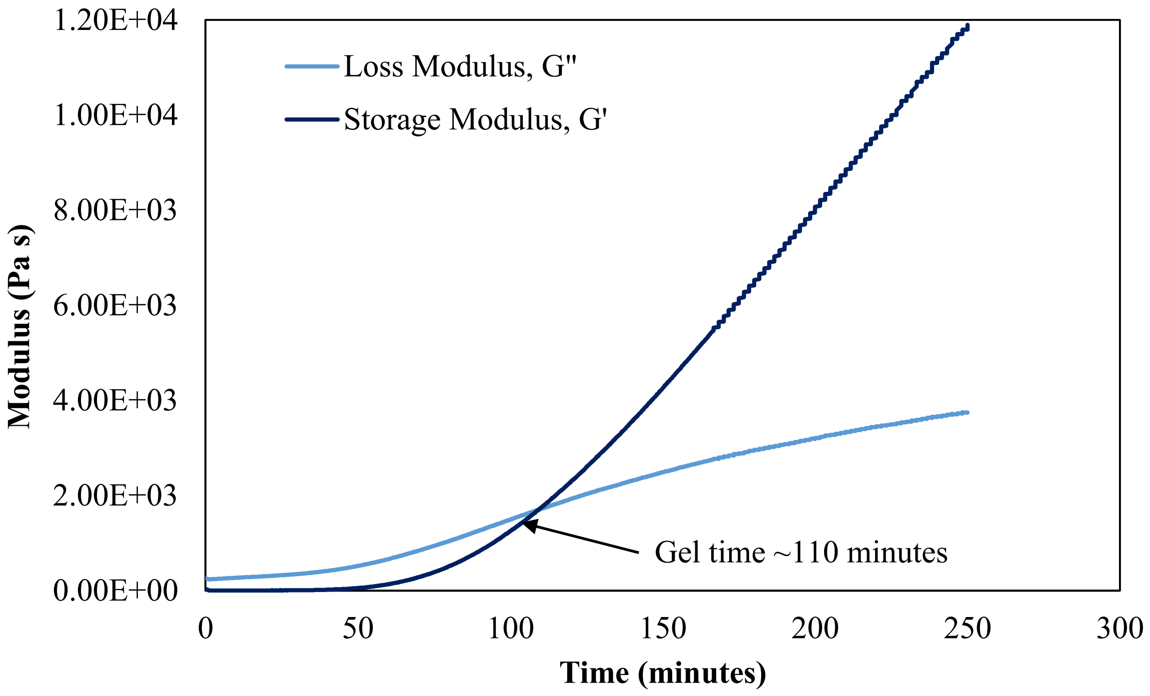


*Figure 35: Curing curves for 1.7 mol IPDI/mol PPG using 2 wt% catalyst.*

Samples of the PU resins (after silane addition) were cured over a period of ~1 week in a silicone tensile bar mold without the use of catalyst. Once a skin had formed on the sample, the bars were able to be removed from the mold and left on a Teflon plate in the lab for additional curing time (~ 15 days) before being tested for their tensile strength. The tensile bars were tested 2-3 weeks after the resins were synthesized to ensure they were cured. For future PU formulations the curing time before testing of tensile bars should be standardized to ensure that all specimens are comparable. The stress-strain data for the resins is shown in Figure 36. The structure of the polyol has been found to be related to the tensile strength of a polyurethane, due to the intermolecular association and crystallization during stretching. In general, polyester polyols result in PUs with higher tensile strengths than polyether polyols.[19] This is consistent with the results of testing the bio-based PUs. It has also been found that in general, polyether polyurethanes have a greater hysteresis compared to polyester polyurethanes.[19] While the hysteresis of the PU samples was not measured, qualitatively it was seen that the PPG PU samples returned to their original length immediately after tensile testing, whereas the Myrinol™ DG-110 PU samples were slower to return to their original length.

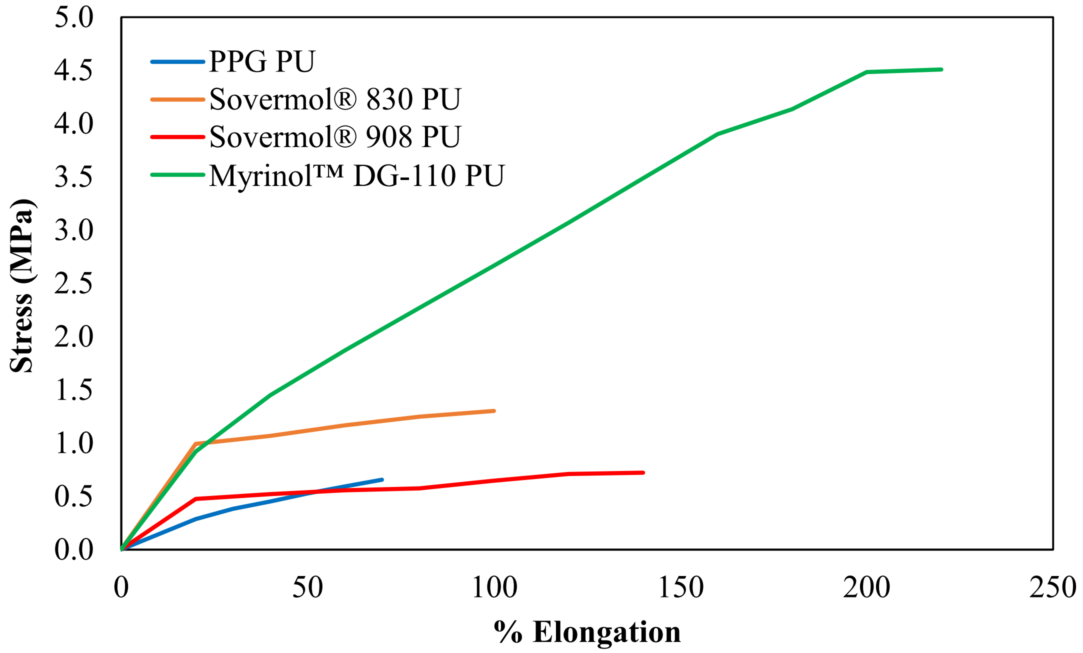


*Figure 36: Stress-strain properties for IPDI/bio-based polyol PUs vs. 1.7 mol IPDI/mol PPG PU.*

While this thesis focussed on producing a PU resin with properties similar to Adfast's 1.7 mol IPDI/mol PPG resin, Adfast has numerous other products for different applications. The product that was being imitated in this research had high elongation and elasticity. Adfast also has adhesive products that require high strength and lower elasticity. A graphical representation of Adfast's different product characteristics is shown in Figure 37. The PUs produced from the Sovermol® polyols were hard and brittle, which is undesirable for sealant applications, however they have potential to be used in an adhesive/coating application based on their properties. Based on the physical properties of the Sovermol® 830 PU (tensile strength = 1.2 MPa , elongation at break = 100%) and Sovermol® 908 PU (tensile strength = 0.6 MPa, elongation at break = 140%) (Table 16), investigation of these formulations for bio-based PUs for sealants was not pursued further in this thesis. The Myrinol™ DG-110 polyol/IPDI showed properties more suited to sealants (tensile strength = 4.8 MPa, elongation at break = 220%). The remaining research covered in this thesis focuses only on the use of the Myrinol™ DG-110 bio-based polyol and the optimization of that system.

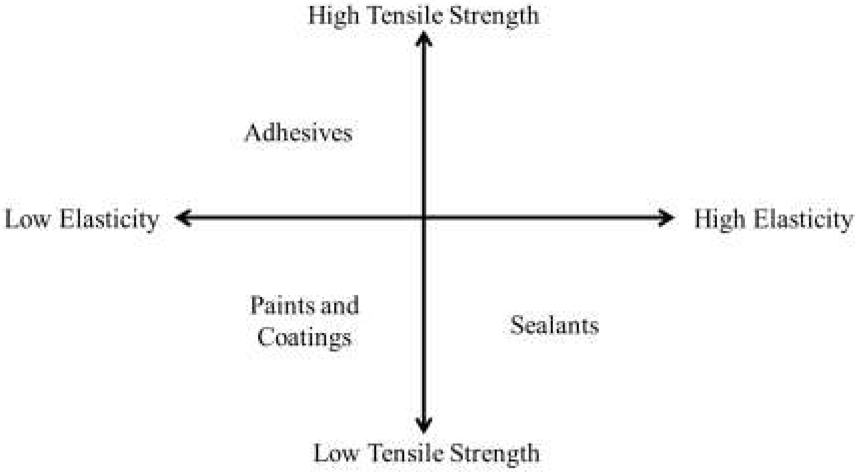


*Figure 37: Graphical representation of Adfast's product markets.*

*Table 16: Summary of physical properties of 1.7 mol IPDI/mol polyol polyurethanes.*

| PU Formulation | Viscosity (Pa s) | Tensile Strength (MPa) | Elongation at Break (%) |
|---|---|---|---|
| 1.7 mol IPDI/mol PPG | 20 | 0.6 ± 0.2 | 60 ± 25 |
| 1.7 mol IPDI/mol Sovermol® 830 | 17,700 | 1.2 ± 0.5 | 100 ± 30 |
| 1.7 mol IPDI/mol Sovermol® 908 | 14,800 | 0.6 ± 0.2 | 140 ± 40 |
| 1.7 mol IPDI/mol Myrinol™ DG-110 | 4,200 | 4.8 ± 0.8 | 220 ± 40 |

## 4.6 OPTIMIZATION OF MYRINOL™ DG-110 POLYOL SYSTEM WITH BIO-BASED ISOCYANATE

From the results discussed already, it was seen that the 1.7 mol IPDI/mol Myrinol™ DG-110 polyol had the most promise to be used in an Adfast sealant. One characteristic that was undesirable was the high viscosity of the resin. The 1.7 mol IPDI/mol Myrinol™ DG-110 PU had a viscosity of 4,200 Pa s, compared to the maximum feasible viscosity that Adfast can mix being 2,000 Pa s. In order to both improve the physical properties of the Myrinol™-based PU and increase the bio-based content of the final product, the substitution of a bio-based isocyanate in the place of IPDI was investigated. It was hypothesized that using LDI instead of IPDI could lower the viscosity of the resin based on the more linear structure of LDI compared to IPDI. In terms of the soft segment/hard segment polyurethane structure (see Figure 38), having a linear, more flexible diisocyanate, the polyurethane would be expected to have a lower viscosity and more elastic mechanical properties.

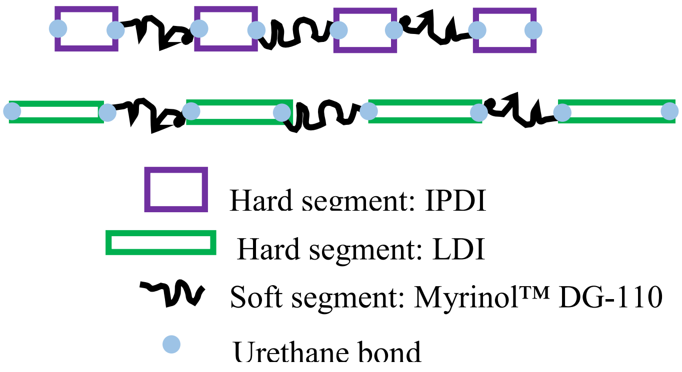


*Figure 38: Graphical explanation of soft and hard segments.*

When 1.7 mol LDI/mol Myrinol™ DG-110 was combined under the standard reaction conditions (following procedure detailed in Table 2), the reaction proceeded very quickly and was only allowed to continue for 20 minutes due to the very high viscosity of the resin and the loss of stirring in the reactor. The normalized GPC traces over the course of this reaction are shown below in Figure 39. The molecular weight after 20 minutes of reaction was found to be 6,100 g/mol (based on PMMA standard calibration).

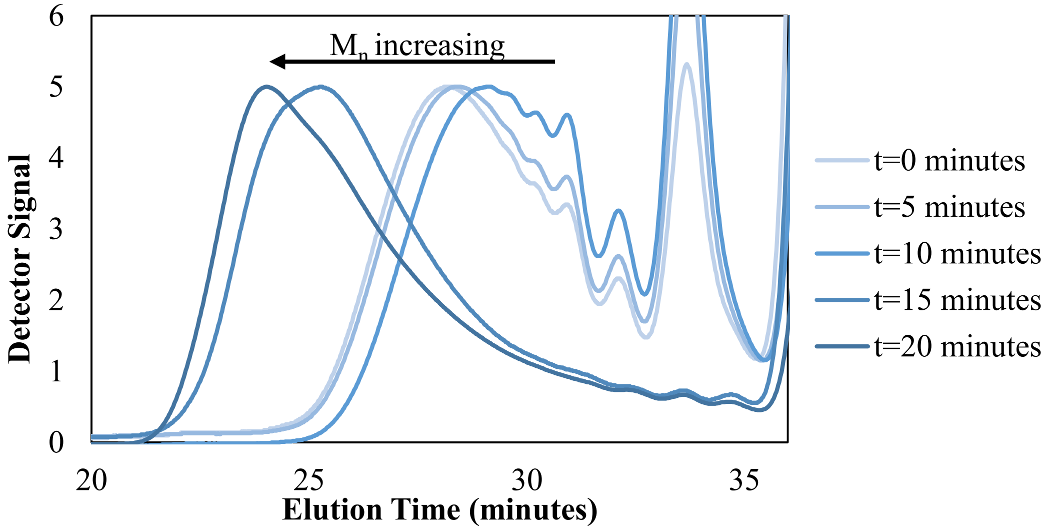


*Figure 39: Normalized GPC traces for 1.7 mol LDI/mol Myrinol™ DG-110 PU with catalyst.*

A second experiment was conducted using LDI and Myrinol™ DG-110, this time without the use of any catalyst to drive the reaction. In this case, the reaction proceeded with much more control and produced the normalized GPC traces seen in Figure 40 over 180 minutes of reaction time. The molecular weight of the resin was found to be 3,000 g/mol after 180 minutes. Based on the integration of the GPC traces and the molecular weights of the resins, it was calculated that the resin was composed of mainly polymers with one Myrinol™ DG-110 unit.

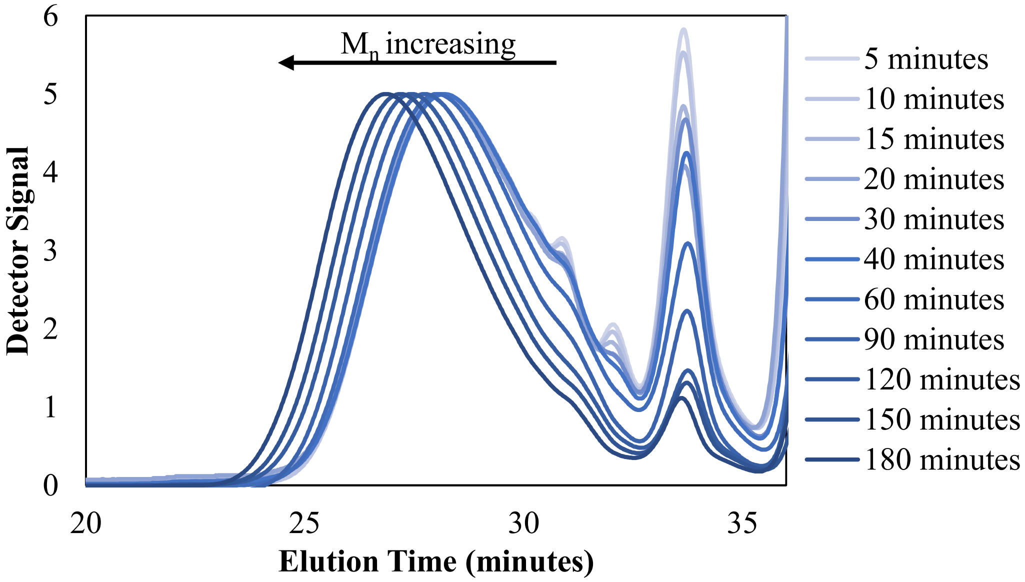


*Figure 40: Normalized GPC traces for 1.7 mol LDI/mol Myrinol™ DG-110 PU without use of catalyst.*

When compared to the reaction of 1.7 mol IPDI/mol Myrinol™ DG-110 (see Figure 41), the 1.7 mol LDI/mol Myrinol™ DG-110 (no catalyst used) reaction rate is similar. Both reactions use the Myrinol™ DG-110™ polyol (GPC $M_n$ = 1,400 g/mol) and the two isocyanates have the same GPC $M_n$ (600 g/mol). Since the $M_n$ of both resins increase over time at a similar rate, but the LDI/Myrinol™ formulation does not use a catalyst, the reactivity of the LDI isocyanate must be greater than that of IPDI. As discussed earlier, the 1.7 mol IPDI/mol Myrinol™ reaction was attempted without the use of catalyst, and it was found that the reaction did not progress at all. No information is available regarding the reactivity of LDI compared to that of IPDI. It is known that the reactivity of the two NCO groups (one primary and one secondary) of IPDI have different reactivity, which could also be true for LDI (also has one primary and one secondary NCO group). In the case of IPDI, when reacted without a catalyst or with dibutyl tin dilaurate the secondary NCO group is more reactive.[64]

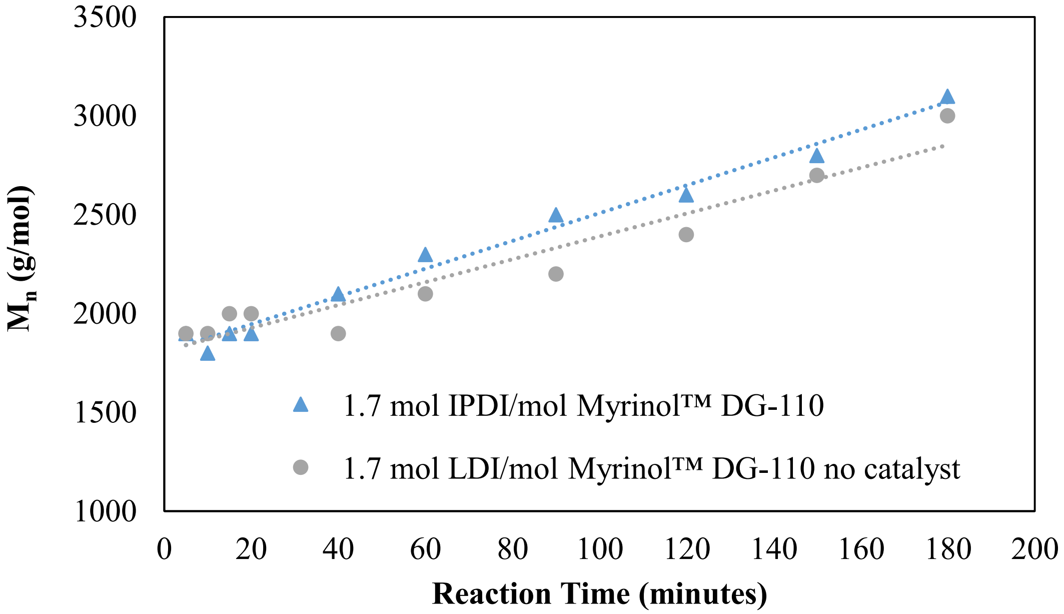


*Figure 41: $M_n$ vs. reaction time for 1.7 mol LDI/mol Myrinol™ DG-110 (no catalyst) and 1.7 mol IPDI/mol Myrinol™ DG-110.*

The viscosity of the 1.7 mol LDI/mol Myrinol™ DG-110 resin was found to be 600 Pa s, significantly lower than the 1.7 mol IPDI/mol Myrinol™ DG-110 resin (4,200 Pa s) (see Figure 42). The two samples that were used to measure the viscosities for the 1.7 mol IPDI/mol Myrinol™ and 1.7 mol LDI/mol Myrinol™ resins had similar molecular weights (~3,000 g/mol), therefore the difference in viscosity is hypothesized to be due to the difference in structure between IPDI and LDI. While the two diisocyanates have almost the same molecular weights ($M_n$, IPDI = 222 g/mol vs. $M_n$, LDI = 226 g/mol), IPDI is cyclic and LDI is linear in structure (see Figure 43).

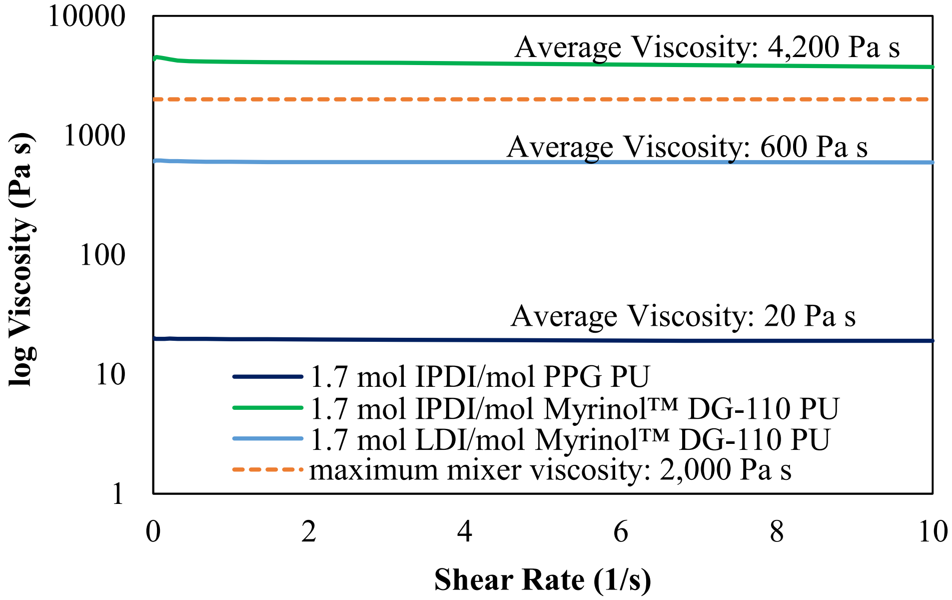
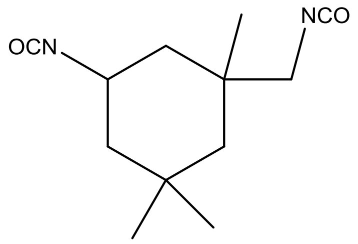
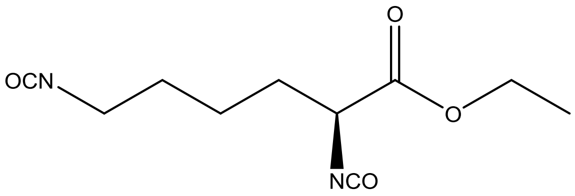


*Figure 42: Viscosities of Myrinol™ DG-110 PU resins at room temperature vs. 1.7 mol IPDI/mol PPG PU.*



IPDI



LDI

*Figure 43: Structures of IPDI and LDI.*

The stress-strain data for the 1.7 mol LDI/mol Myrinol™ DG-110 formulation is shown in Figure 44. The 1.7 mol LDI/mol Myrinol™ DG-110 PU was found to have stress-strain properties similar to the original 1.7 mol IPDI/mol PPG PU. Compared to the 1.7 mol IPDI/mol Myrinol™ DG-110 PU, the replacement of IPDI with LDI decreased the tensile strength and elongation at break. While all three samples shown in Figure 44 are elastic, the IPDI/Myrinol™ PU has much higher toughness (larger area under the stress-strain curve).

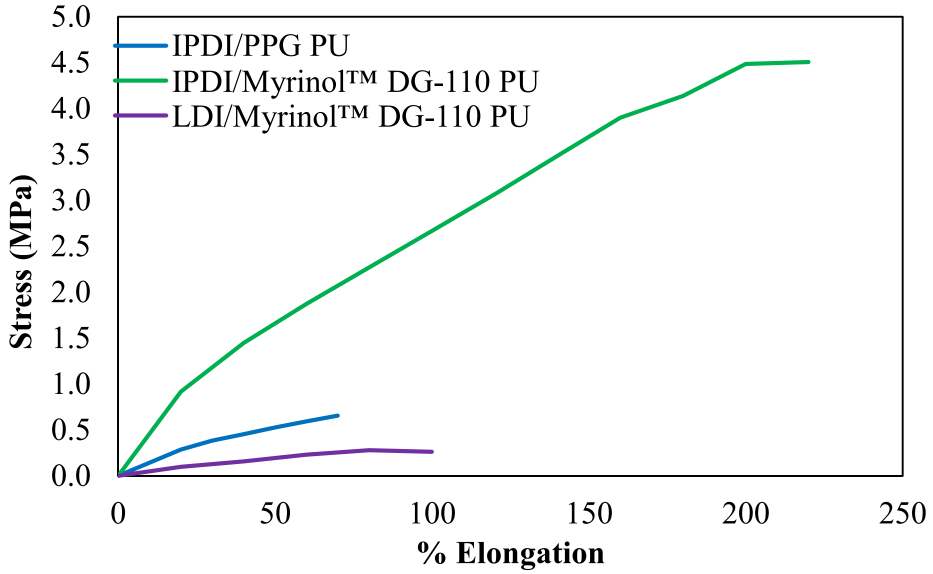


*Figure 44: 1.7 mol LDI/mol Myrinol™ DG-110 vs. 1.7 mol IPDI/mol PPG and 1.7 mol IPDI/mol Myrinol™ DG-110 stress-strain properties.*

Hysteresis testing was not performed, however it can be seen visually in Figure 45 that the IPDI/PPG, IPDI/Myrinol™ DG-110, and LDI/Myrinol™ DG-110 PUs all returned to their original length after tensile testing. An example of a test that could be performed to investigate the hysteresis of the PUs is a cyclic tensile test. This would produce a hysteresis loop and the energy loss due to the viscoelasticity of the resin could be estimated. The defects present in the 1.7 mol LDI/mol Myrinol™ DG-110 tensile bars are due to the silicone mold that the bars were cured in. While the defects were present in the top/bottom sections of the bars (where the clamps hold the samples while testing), there were no defects in the middle section of the bars that would affect the stress-strain measurements.

1.7 mol IPDI/mol PPG PU

1.7 mol IPDI/mol Myrinol™ DG-110 PU

1.7 mol LDI/mol Myrinol™ DG-110 PU

*Figure 45: Tensile bars after testing: bars returned to their original shape.*

Based on the physical properties of the 1.7 mol LDI/mol Myrinol™ DG-110 PU (see Table 17) it shows potential to be used as a sealant product by Adfast, however using a bio-based isocyanate at a large scale is the limitation of this formula. There are currently no commercial suppliers of bio-based isocyanates at the scale required by Adfast. For Adfast to pursue a PU with a bio-based diisocyanate at this time the bio-based diisocyanate would have to be produced in house.

*Table 17: Summary of properties for 1.7 mol LDI/mol Myrinol™ DG-110 without catalyst PU compared to other PU resins.*

| PU Formulation | Viscosity (Pa s) | Tensile Strength (MPa) | Elongation at Break (%) |
|---|---|---|---|
| 1.7 mol IPDI/mol PPG | 20 | 0.6 ± 0.2 | 60 ± 25 |
| 1.7 mol IPDI/mol Sovermol® 830 | 17,700 | 1.2 ± 0.5 | 100 ± 30 |
| 1.7 mol IPDI/mol Sovermol® 908 | 14,800 | 0.6 ± 0.2 | 140 ± 40 |
| 1.7 mol IPDI/mol Myrinol™ DG-110 | 4,200 | 4.8 ± 0.8 | 220 ± 40 |
| 1.7 mol LDI/mol Myrinol™ DG-110 | 600 | 0.3 ± 0.1 | 90 ± 20 |

## 4.7 FUTURE WORK

While this thesis has led to the synthesis of polyurethanes from bio-based components that show promise to be incorporated into a sealant, there is still further optimization and testing required. The viscosity and stress-strain properties of both the 1.7 mol IPDI/mol Myrinol™ DG-110 (viscosity = 4,200 Pa s, tensile strength = 4.8 MPa, elongation at break = 220%) and 1.7 mol LDI/mol Myrinol™ DG-110 (viscosity = 600 Pa s, tensile strength = 0.3 MPa, elongation at break = 90%) formulations show promise to be suitable for sealants, but there are still issues with both of these resins that need to be addressed. The PUs produced from the Sovermol® polyols were found to be too hard and brittle for sealant products, but in the future Adfast may be interested in revisiting these formulations for adhesive or coating applications.

The high viscosity of the 1.7 mol IPDI/mol Myrinol™ DG-110 resin is an issue in terms of scale-up. The maximum viscosity that Adfast can mix in their reactor is 2,000 Pa s, however the desirable range is 10-500 Pa s. The viscosity of the 1.7 mol IPDI/mol Myrinol™ DG-110 was found to be 4,800 Pa s, which is too high to be scaled up by Adfast. The addition of a plasticizer could lower the viscosity to make this resin feasible. Because the IPDI/Myrinol™ resin shows promising stress-strain properties, lowering the viscosity should be investigated.

The issue with the 1.7 mol LDI/mol Myrinol™ DG-110 PU is the price and availability of LDI, and in general any bio-based isocyanate. The economic feasibility of using bio-based components, Myrinol™'s DG-110 polyol and LDI, must also be assessed. From Adfast's purchasing department, PPG and IPDI cost $4.70 CAD/kg and $15.00 CAD/kg respectively when purchased in bulk by Adfast. Myrinol™ DG-110 is priced at $3.20 CAD/kg ($1.10 USD/lb) which is competitive with the price of PPG. The price of LDI used in this project ($66.00 CAD/5 g), when used only on a small scale, is much too high to be applied at a commercial scale. There are no large-scale suppliers of bio-based isocyanates, and synthesizing bio-based isocyanates at a commercial scale poses many challenges due to dangerous synthesis methods (nitrenes, azides or phosgene), even when using bio-based materials.[17]

Adfast is interested in performing a scale-up of a bio-based PU at their facility, once a formula has been reached with a low enough viscosity to be handled by their mixer. This PU resin (20-60% of final product) would be blended with UV/oxidation stabilizers (< 3%), plasticizer (5-30%), calcium carbonate (5-40%), pigment (< 5%), silica (< 15%) and catalyst (< 5%) and could be tested as a sealant end-product. Adfast tests the properties of their sealants using a series of Instron tests. From the Instron machine they measure the elongation, tensile strength and modulus of samples. Lapshear assemblies are also prepared and tested with the Instron to determine the adhesion of the sealants. To determine the stability of sealant formulations, the samples are exposed to conditions such as water immersion, freezing, salt spraying, UV radiation and heat and are then tested using the Instron.

One other parameter that has not been assessed for the bio-based PUs is the curing time and the effect of the curing catalyst that Adfast currently uses. Qualitatively, curing has been observed over long periods of time (~15 days), but there has been no precise measurement of the curing time, shelf life, etc. of the bio-based PUs when catalyst is used. This should be assessed before a scale-up to ensure that the bio-based PUs are capable of curing in a reasonable amount of time when catalyst is added. While the curing time is largely dependent on the amount of catalyst added to the resin, it should be verified that the curing mechanism (atmospheric moisture's reaction with the silane-functionalized end-capper) behaves the same for the bio-based formulations.

Going forward, there are three options within the diisocyanate/polyol synthesis route for Adfast to consider. By mass%, the polyol makes up the majority of the PU resin, therefore replacing the petroleum-based PPG with a bio-based polyol is the logical first step to scale-up. The prospect of Adfast synthesizing their own bio-based polyols from raw bio-sourced oils is of interest as an alternative to using a commercial bio-based polyol. Alternate commercial bio-based polyols should be assessed, as well as synthesis methods in order for Adfast to produce their own bio-based polyols on a large scale. While this would still involve a petroleum-based isocyanate (derived through the use of phosgene) it would result in a project with a high renewable content and would likely have an economical benefit to Adfast due to the low price of bio-based polyols. By incorporating a bio-based isocyanate, the renewable content of the product would increase to close to 100%, however the large-scale synthesis of bio-based isocyanates comes with many issues, and there are currently no commercial providers of bio-based isocyanates on an industrial scale. Adfast could also produce their own bio-based isocyanates internally, and do so without using phosgenation. This would involve the scale-up of Curtius, Hofmann or Lossen rearrangements, which has not been explored due to the involvement of nitrenes and acyl azides in the process. The dangers of phosgene versus acyl azides should be assessed to determine if the pursuit of non-phosgene isocyanates at large scale has merit. From a green perspective, this option is currently seen as the most beneficial as it eliminates all reliance on petroleum resources and does not involve toxic phosgene in the synthesis process. However, even this product still involves an isocyanate. Regardless of the bio-based nature, isocyanates are still toxic and require extreme care in large scale production. These three options are summarized graphically in

Figure *46*.

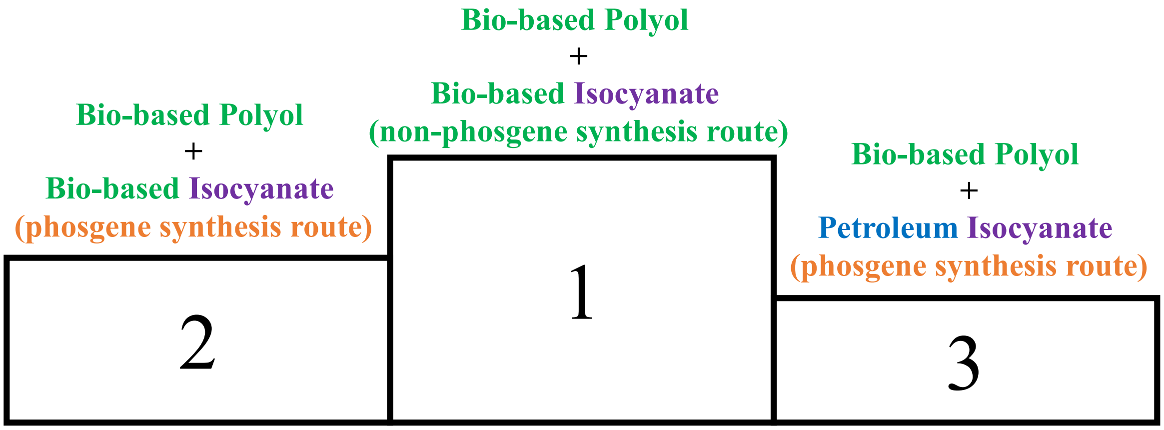


*Figure 46: Potential future Adfast PU resins using polyols/isocyanates, ranked in order of effectiveness from a green perspective.*

In order to avoid isocyanates completely, an entirely different approach: using dicarbonates and diamines to produce non-isocyanate polyurethanes (NIPUs) is also being considered by McGill and Adfast. These can both be bio-based, and the synthesis of dicarbonates involves $CO_2$ as a reactant, another green aspect of this method. If this route is followed, Adfast could have a completely bio-based NIPU that involves no phosgene, isocyanate or other toxic reactants. This method of preparing NIPUs is in preliminary stages of research in parallel with the bio-based polyol/diisocyanate method. Both of these routes should be pursued, and through one or both of them, McGill may be able to provide Adfast with an economical, non-petroleum based and green product.

# 5.0 CONCLUSION

The main purpose of this thesis was to investigate the possibility of substituting bio-based components into an existing industrial polyurethane base resin made from petroleum-sourced building blocks. In order to compare bio-based PU resins to the original product, the original formula had to be replicated on a small scale and studied before measuring its physical properties. The analysis of the molecular weight distribution of the PU lead to the discovery that dimers and trimers were present, in addition to the chains containing only one PPG monomer (reacted with two moles of IPDI) that Adfast was expecting. It was concluded that by decreasing the molar ratio of IPDI/PPG, the number of PPG units in the polymer could be increased. This is valuable new information for Adfast that can help them to tailor the properties of their resins going forward. Values for the viscosity (20 Pa s) and stress-strain properties (elongation at break = 60%, break stress = 0.6 MPa) were gathered, were used as benchmarks to compare the bio-based PUs developed during this project, and will continue to be used as comparisons for new bio-based PU formulas going forward.

A selection of commercial bio-based polyols was then evaluated and used to make bio-based PU resins by substituting the polyol portion of Adfast's formulation. The viscosity and stress-strain properties were gathered for these new bio-based resins and compared to the benchmark of Adfast's original PU formulation. The two PU resins derived from Sovermol® polyols, Sovermol® 830 and Sovermol® 908, with IPDI were found to have higher break stresses (1.2 MPa and 0.6 MPa respectively), but were hard and brittle, making them poor candidates for the desired sealant application. These polyols may be assessed for alternate applications such as adhesives or coatings.

After seeing promising results with polyurethanes produced from the Myrinol™ DG-110 polyol with IPDI (viscosity = 4,200 Pa s, break stress = 4.8 MPa, elongation at break = 220%), this system was further studied by inserting the bio-based diisocyanate, LDI, instead of the original petroleum based diisocyanate IPDI. This all bio-based system was notable by not requiring catalyst for the polymerization to proceed. By substituting LDI for IPDI, the viscosity of the resin before curing became lower (600 Pa s), and the cured resin exhibited lower elongation at break (90%) and break stress (0.3 MPa). The stress-strain properties of the LDI/Myrinol™ PU were most similar (vs. the other PUs produced during this project) to those of the original IPDI/PPG PU.

Both the 1.7 mol IPDI/mol Myrinol™ DG-110 formulation and the 1.7 mol LDI/mol Myrinol™ DG-110 formulation show promise to be included in Adfast's product line. The viscosity of the 1.7 mol IPDI/mol Myrinol™ DG-110 is too currently too high for Adfast to handle at a large scale, but the incorporation of a plasticizer could reduce this viscosity. Further testing including adhesion, UV resistance, and scale up/blending of this resin is necessary to determine if either of these formulations would result in a suitable sealant product. The economics of using bio-based components must also be investigated: compared to PPG, Myrinol™ DG-110 is available at a competitive price ($ 4.70 CAD/kg, PPG vs. $3.20 CAD/kg, Myrinol™ DG-110), however incorporating a bio-based isocyanate is currently infeasible as there are no bulk suppliers of LDI or any other bio-based isocyanates.

This project has paved the way for Adfast and the Maric lab to collaborate on many new polyurethane formulations and potential commercial products. The incorporation of bio-based polyols into the formulation was tested, showed promise, and should be explored further, perhaps with alternative bio-based polyols. A PU from a bio-based polyol and a petroleum-based diisocyanate will have a high renewable content since the polyol makes up a majority of the mass of the resin. Different commercial polyols should be explored as well as the large-scale production of bio-based polyols from raw feedstocks—which could also give Adfast an economic advantage. By using both a bio-based polyol and diisocyanate, the renewable content of the PU would be even higher, but the process would still include an isocyanate and phosgene. The bio-based isocyanate, since not available commercially at a large scale yet, would have to be produced by Adfast. If a bio-based isocyanate could be synthesized via a phosgene-free route, then Adfast could have a product with very high renewable content, and a significantly greener process, however at the end of the day there is still an isocyanate in the process. The alternative pathway is to pursue NIPUs, which can meet the renewable content, non-phosgene, and non-isocyanate desires of Adfast. Regardless of which direction Adfast decides to go in the future, this thesis has opened the door to multiple different options that could result in a green and economically competitive product.

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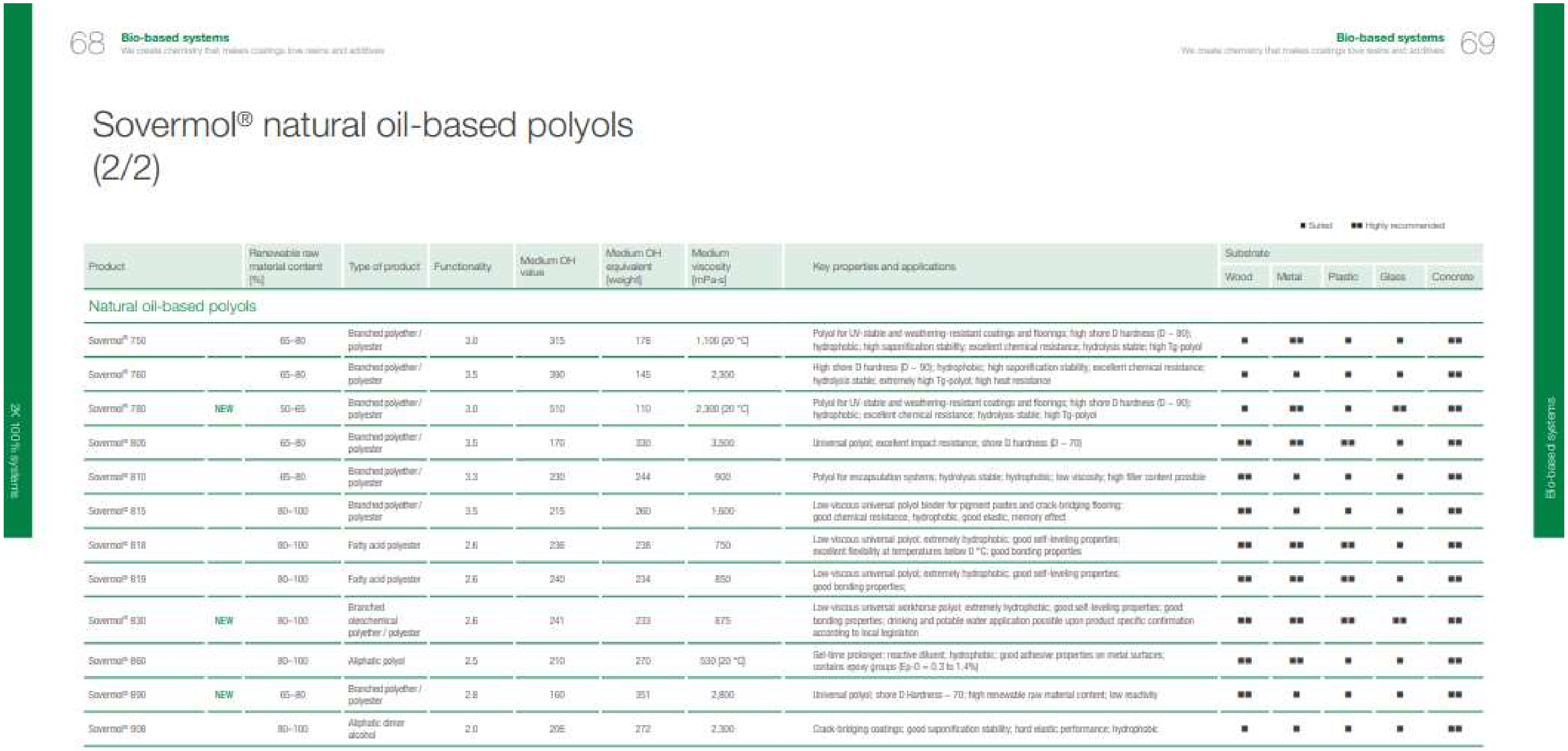
# 7.0 APPENDIX A

Data sheet containing Sovermol® 830 properties.



68 **Bio-based systems**
We create chemistry that makes coatings love resins and additives

**Bio-based systems** 69
We create chemistry that makes coatings love resins and additives

## Sovermol® natural oil-based polyols (2/2)

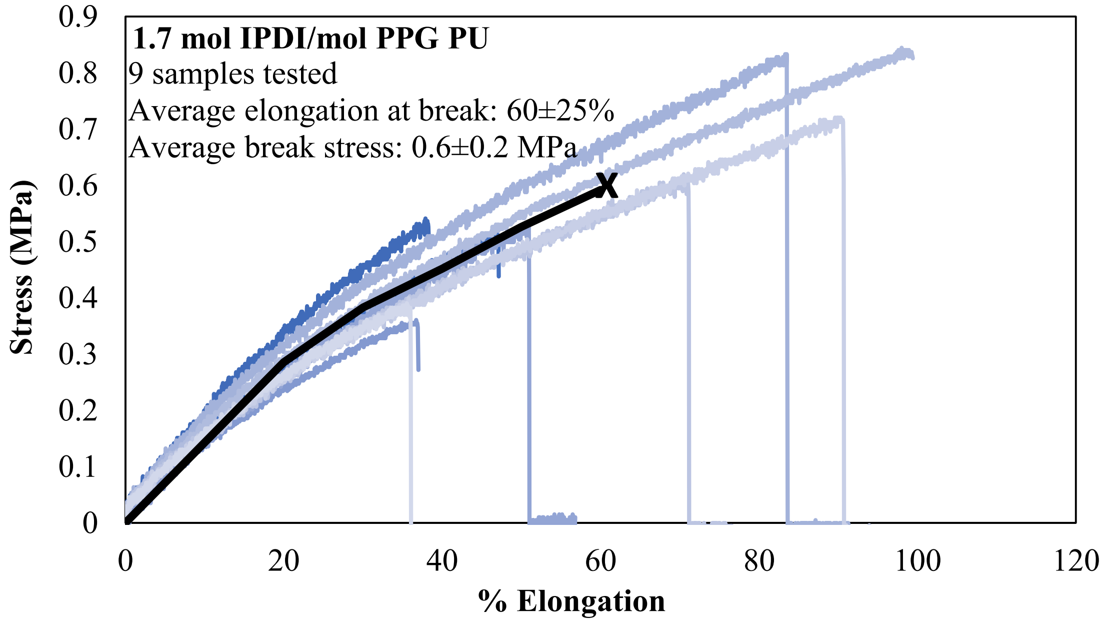
■ Suited ■■ Highly recommended

| Product | | Renewable raw material content [%] | Type of product | Functionality | Medium OH value | Medium OH equivalent [weight] | Medium viscosity [mPa·s] | Key properties and applications | Substrate | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Wood | Metal | Plastic | Glass | Concrete |
| Natural oil-based polyols | | | | | | | | | | | | | |
| Sovermol® 750 | | 65–80 | Branched polyether / polyester | 3.0 | 315 | 178 | 1,100 (20 °C) | Polyol for UV-stable and weathering-resistant coatings and floorings; high shore D hardness (D ~ 80); hydrophobic; high saponification stability; excellent chemical resistance; hydrolysis stable; high Tg-polyol | ■ | ■■ | ■ | ■ | ■■ |
| Sovermol® 760 | | 65–80 | Branched polyether / polyester | 3.5 | 390 | 145 | 2,300 | High shore D hardness (D ~ 90); hydrophobic; high saponification stability; excellent chemical resistance; hydrolysis stable; extremely high Tg-polyol; high heat resistance | ■ | ■ | ■ | ■ | ■■ |
| Sovermol® 780 | NEW | 50–65 | Branched polyether / polyester | 3.0 | 510 | 110 | 2,300 (20 °C) | Polyol for UV-stable and weathering-resistant coatings and floorings; high shore D hardness (D ~ 90); hydrophobic; excellent chemical resistance; hydrolysis stable; high Tg-polyol | ■ | ■■ | ■ | ■■ | ■■ |
| Sovermol® 805 | | 65–80 | Branched polyether / polyester | 3.5 | 170 | 330 | 3,500 | Universal polyol; excellent impact resistance; shore D hardness (D ~ 70) | ■■ | ■■ | ■■ | ■ | ■■ |
| Sovermol® 810 | | 65–80 | Branched polyether / polyester | 3.3 | 230 | 244 | 900 | Polyol for encapsulation systems; hydrolysis stable; hydrophobic; low viscosity; high filler content possible | ■■ | ■ | ■ | ■ | ■■ |
| Sovermol® 815 | | 80–100 | Branched polyether / polyester | 3.5 | 215 | 260 | 1,600 | Low-viscous universal polyol binder for pigment pastes and crack-bridging flooring; good chemical resistance, hydrophobic, good elastic, memory effect | ■■ | ■ | ■ | ■ | ■■ |
| Sovermol® 818 | | 80–100 | Fatty acid polyester | 2.6 | 236 | 238 | 750 | Low-viscous universal polyol; extremely hydrophobic; good self-leveling properties; excellent flexibility at temperatures below 0 °C; good bonding properties | ■■ | ■■ | ■■ | ■ | ■■ |
| Sovermol® 819 | | 80–100 | Fatty acid polyester | 2.6 | 240 | 234 | 850 | Low-viscous universal polyol; extremely hydrophobic; good self-leveling properties; good bonding properties; | ■■ | ■■ | ■■ | ■ | ■■ |
| Sovermol® 830 | NEW | 80–100 | Branched oleochemical polyether / polyester | 2.6 | 241 | 233 | 875 | Low-viscous universal workhorse polyol; extremely hydrophobic; good self-leveling properties; good bonding properties; drinking and potable water application possible upon product specific confirmation according to local legislation | ■■ | ■■ | ■■ | ■■ | ■■ |
| Sovermol® 860 | | 80–100 | Aliphatic polyol | 2.5 | 210 | 270 | 530 (20 °C) | Gel-time prolonger; reactive diluent; hydrophobic; good adhesive properties on metal surfaces; contains epoxy groups (Ep-O ~ 0.3 to 1.4%) | ■■ | ■■ | ■ | ■ | ■■ |
| Sovermol® 890 | NEW | 65–80 | Branched polyether / polyester | 2.8 | 160 | 351 | 2,800 | Universal polyol; shore D Hardness ~ 70; high renewable raw material content; low reactivity | ■■ | ■ | ■ | ■ | ■■ |
| Sovermol® 908 | | 80–100 | Aliphatic dimer alcohol | 2.0 | 205 | 272 | 2,300 | Crack-bridging coatings; good saponification stability; hard elastic performance; hydrophobic | ■ | ■ | ■ | ■ | ■■ |

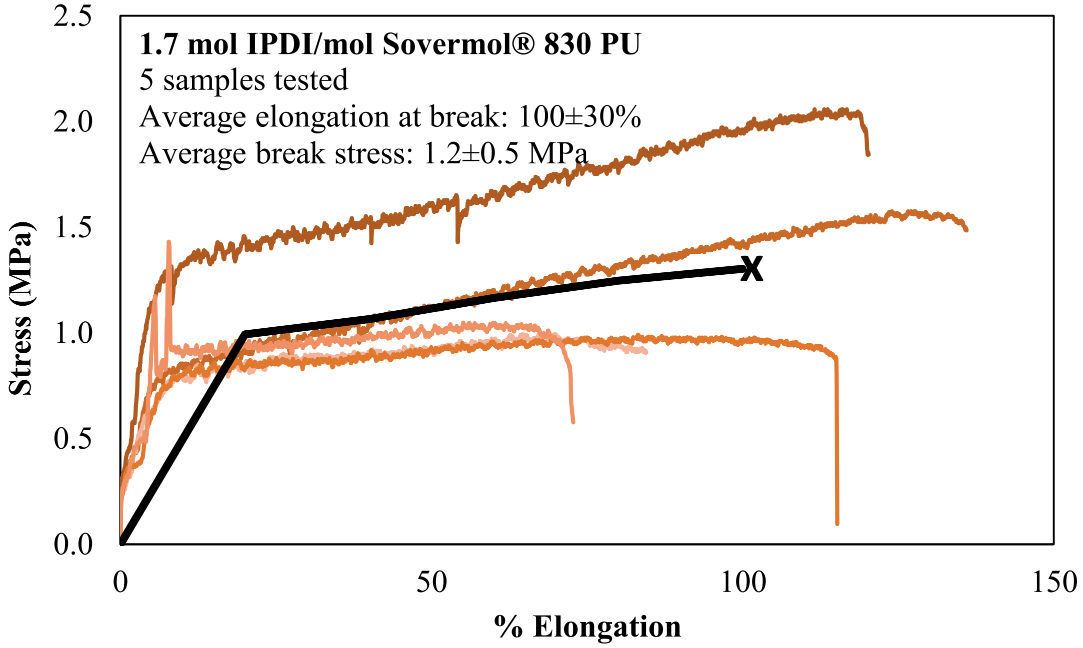
# 8.0 APPENDIX B

## Stress-strain Data

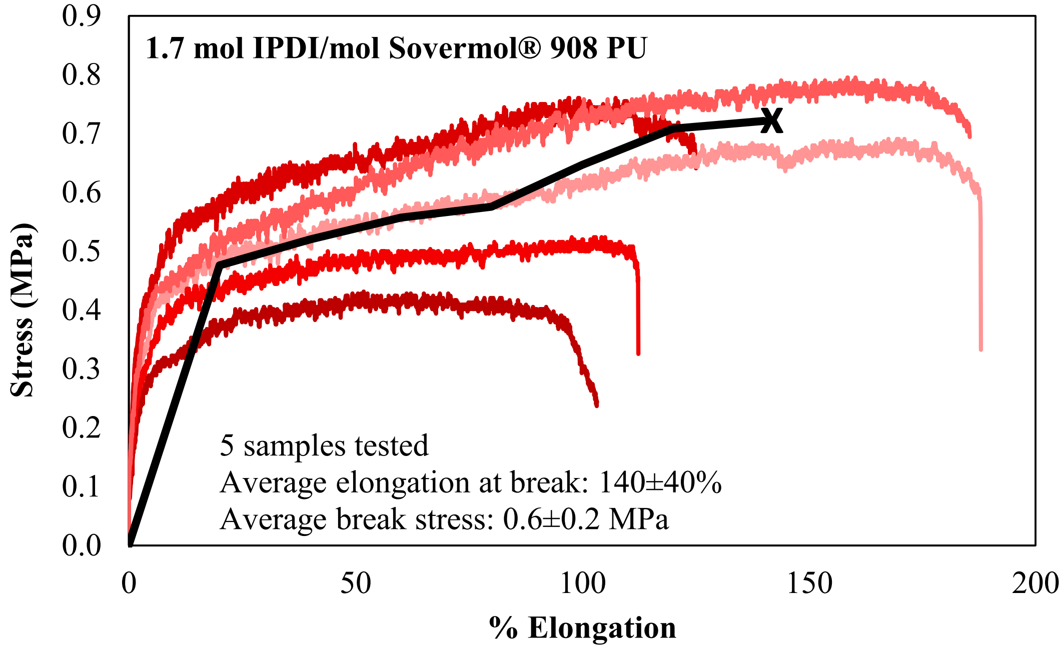
For each PU formulation, multiple tensile bars were tested and an average of all data sets was used as a representative curve in the body of the thesis. Below, all raw data sets are shown with the average representative curves.



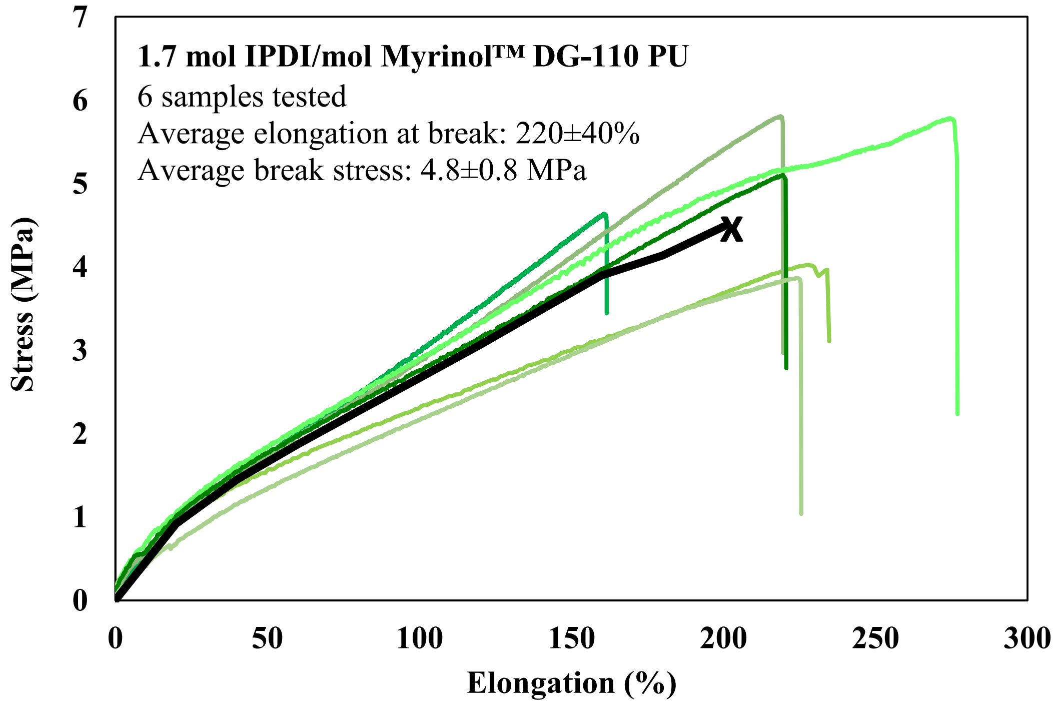
Raw stress-strain data for 1.7 mol IPDI/mol PPG tensile bars.



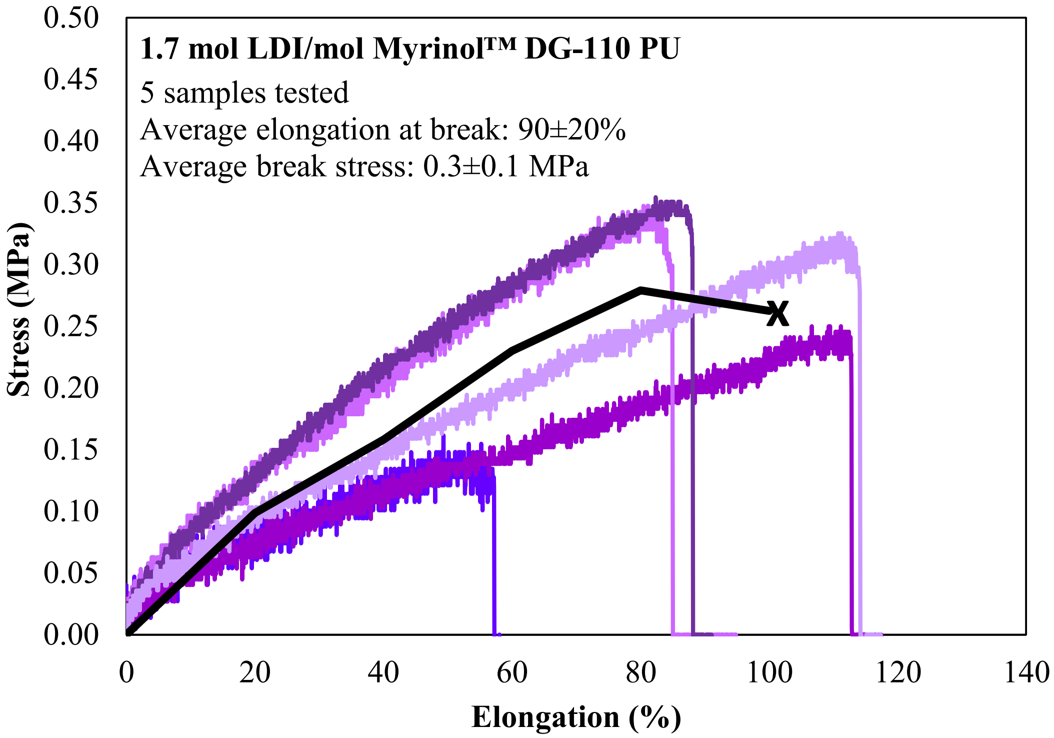
Raw stress-strain data for 1.7 mol IPDI/mol Sovermol® 830 tensile bars.



Raw stress-strain data for 1.7 mol IPDI/mol Sovermol® 908 tensile bars.



Raw stress-strain data for 1.7 mol IPDI/mol Myrinol™ DG-110 tensile bars.



Raw stress-strain data for 1.7 mol LDI/mol Myrinol™ DG-110 tensile bars.