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THE EFFECT OF POSS FILLERS IN NON-ISOCYANATE POLYURETHANE HYBRID RESINS

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Submitted by:

Carlee MacInnis

Department of Chemical Engineering
McGill University
Montréal, Quebec, Canada

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ABSTRACT

Polyurethanes (PUs) are one of the most versatile classes of polymers that have applications in many industrial sectors such as medical, automotive, and insulation. However, conventional PUs are typically synthesized via a polyaddition reaction of diols (polyols) and diisocyanates, which involves the use of lethal phosgene gas. Not only is the phosgene gas used to produce isocyanates toxic, but the isocyanates themselves also pose a significant risk to health and safety. Therefore, due to the rising importance of ensuring the safety of workers and consumers, as well as the growing concerns for the environment, new ways to create polyurethanes without the use of toxic isocyanates have emerged. Through using non-toxic and renewable resources, researchers have been able to develop Non-Isocyanate Polyurethanes (NIPU) in recent years.

NIPUs known as polyhydroxyurethanes (PHUs) can be synthesized via a polyaddition reaction between a polycyclic carbonate and a polyamine. However, some key challenges hinder the ability of PHUs to be transferred to industrial scale, such as inferior mechanical and chemical properties as well as slower polymerization rates as compared to PUs. To overcome these limitations, inorganic/organic materials can be added with PHUs to create a hybrid PHU (HPHU), which is the focus of this thesis. Specifically, polyhedral oligomeric silsesquioxane (POSS) are added to PHU prepolymers to create HPHUs with enhanced mechanical and thermal properties. These hybrid materials can then be further functionalized with moisture-curable groups to obtain a final cured film comparable to conventional PUs.

The incorporation of POSS into PHU prepolymers to obtain HPHUs was found to be successful through GPC, FTIR and NMR characterization methods. Furthermore, the thermal degradation of the HPHUs was significantly improved with increasing POSS concentration compared to their PHU counterparts. However, the HPHU T_g values remained relatively similar to the PHU polymers. The steady shear viscosity was also investigated and an increase in viscosity was observed for the HPHUs and fell within a desirable range suitable for scaleup.

The PHUs and HPHUs were then further functionalized with 3-Isocyanatopropyl (trimethoxy) silane (IPTMS) via the pendant hydroxyl bonds within the backbone of the polymers. This allowed

the polymers to cure in ambient conditions within 24 h to obtain final cross-linked films. FTIR confirmed that no unreacted isocyanates were remaining in the film and also revealed that the incorporation of IPTMS into the polymer network was successful. Subsequent gel content tests in THF, water, and toluene were performed and excellent gel contents of 87-99% in THF were observed for the cured films. Additionally, water swelling and contact angle tests confirmed that the POSS-modified films exhibited hydrophobic behavior. Finally, thermal and mechanical properties were investigated. It was found that there were only minimal increases in thermal degradations for the HPHUs films compared to the PHUs, and no difference in the T_g values. Conversely, the mechanical properties showed positive differences. The Young's modulus and tensile strength were improved with increasing POSS concentration and good elongations at break were observed. When compared to a conventional PU sealant, the HPHU achieved a tensile strength that was two-fold and a comparable elongation at break. Overall, the HPHUs formulated in this work are found to be suitable candidates to replace current PU sealants.

RÉSUMÉ

Les polyuréthanes (PUs) sont l'une des classes de polymères les plus polyvalentes ayant des applications dans de nombreux secteurs industriels tels que les secteurs du médical, de l'automobile et de l'isolation. Cependant, les PUs conventionnels sont généralement synthétisés par une réaction de polyaddition de polyols (principalement de diols) et de diisocyanates. Ces derniers impliquent l'utilisation de gaz phosgène mortel pour leur fabrication. Non seulement le gaz phosgène utilisé pour produire les isocyanates est toxique, mais les isocyanates eux-mêmes présentent également un risque important pour la santé et la sécurité. C'est pourquoi, en raison de l'importance croissante de la sécurité des travailleurs et des consommateurs, ainsi que des préoccupations pour l'environnement, de nouvelles méthodes de fabrication de polyuréthanes sans l'utilisation d'isocyanates ont vu le jour. En utilisant des ressources non toxiques et renouvelables, les chercheurs ont pu développer des polyuréthanes sans isocyanate (NIPUs) ces dernières années.

Certains NIPUs, appelés polyhydroxyuréthanes (PHU), peuvent être synthétisés par une réaction de polyaddition entre un carbonate polycyclique et une polyamine. Cependant, certains défis majeurs entravent la capacité des PHUs à être transférés à l'échelle industrielle, tels que des propriétés mécaniques et chimiques inférieures ainsi que des taux de polymérisation plus faibles par rapport aux PUs. Pour surmonter ces limitations, des matériaux inorganiques/organiques peuvent être ajoutés aux PHUs afin de former des PHUs hybrides (HPHUs), qui font l'objet de cette thèse. Plus précisément, le silsesquioxane oligomère polyédrique (POSS) est ajouté aux prépolymères de PHU pour créer des HPHUs avec des propriétés mécaniques et thermiques améliorées. Ces matériaux hybrides peuvent ensuite être fonctionnalisés avec des groupes réticulant à l'humidité pour obtenir un film dur final comparable aux PUs conventionnels.

L'incorporation de POSS dans des prépolymères de PHU pour obtenir des HPHUs s'est avérée réussie grâce aux méthodes de caractérisation GPC, FTIR et NMR. De plus, la dégradation thermique des HPHUs a été significativement améliorée avec l'augmentation de la concentration de POSS par rapport à leurs homologues PHUs. Cependant, les valeurs de température de transition vitreuse (T_g) des HPHUs sont restées relativement similaires à celles des polymères PHUs. La viscosité à cisaillement constant a également été étudiée et une augmentation de la viscosité a été observée pour les HPHUs.

Les PHUs et HPHUs ont ensuite été fonctionnalisés avec du 3-isocyanatopropyl triméthoxy silane (IPTMS) via les liaisons hydroxyle pendantes du squelette des polymères. Cela a permis aux polymères de réticuler dans des conditions ambiantes en 24 heures pour obtenir des films réticulés finaux. L'analyse FTIR a confirmé qu'il ne restait pas d'isocyanate non réagissant dans le film et a également révélé que l'incorporation de l'IPTMS dans le polymère était réussie. Des tests ultérieurs de contenu de gel dans le THF, l'eau et le toluène ont été effectués et d'excellents taux de gel de 87-99% dans le THF ont été observés pour les films après réticulation. De plus, des tests de gonflement d'eau et d'angle de contact ont confirmé que les films modifiés par le POSS présentaient un comportement hydrophobe. Enfin, les propriétés thermiques et mécaniques ont été étudiées. Il a été constaté qu'il n'y avait que des augmentations minimales des dégradations thermiques pour les films HPHUs par rapport aux PHUs, et aucune différence dans les valeurs T_g . Par contre, les propriétés mécaniques ont montré des différences positives. Le module d'Young et la résistance à la traction ont été améliorés avec l'augmentation de la concentration de POSS et de bons allongements à la rupture ont été observés. Par rapport à un mastic PU classique, PHU a atteint une résistance à la traction deux fois supérieure et un allongement à la rupture comparable. Dans l'ensemble, les HPHUs formulés dans ce travail se sont avérés être des candidats appropriés pour remplacer les scellants PU actuels.

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Mr. Georges Younes provided valuable guidance and support throughout the project as well as perform the following tasks:

- Developed and optimized the DGC synthesis reaction in section 3.2.1.
- Developed the prepolymer synthesis reaction for the Jeffamine D-2000 PHUs in section 3.2.2.
- Aided with FTIR and NMR peak assignments for the PHU prepolymers in sections 4.1.2 and 4.1.3.

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1.0 INTRODUCTION

Since their genesis in the 1930's when discovered by Bayer *et al.*, polyurethanes (PUs) have expanded greatly and are now one of the most versatile classes of polymers [1]. Found ubiquitously in everyday life, PUs are used in sectors such as medical, automotive and insulation materials. In 2017, the worldwide production of all plastics was 348 million tonnes [2], with Asia contributing 50.1% of this global production, Europe contributing 18.5%, and NAFTA at 17.7%. Of the total European production, PUs made up 7.7% thus making them the 6th largest produced plastic [2]. This demand can be attributed to the diversity of synthesis routes that can be taken to produce PUs, which give a range of products with different macromolecular structures [3]. PUs can be classified generally into three different categories: flexible foams, rigid foams, and non-porous materials [3].

Conventional PUs have good mechanical properties, but due to their molecular composition, they suffer from insufficient permeability and have poor hydrolytic stability, making them vulnerable to environmental degradation [4]. Most PUs are typically synthesized via a polyaddition reaction of diols (polyols) and diisocyanates in the presence of tertiary amines as a catalyst [5]. The downside to this reaction, however, arises from the synthesis of the diisocyanates, which involves the use of lethal phosgene gas. Phosgene reacts with amines to produce diisocyanates, with the most commonly used ones being methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) [1, 5]. Not only is the phosgene gas used to produce these isocyanates toxic, but the isocyanates themselves also pose a significant risk to health and safety and are considered as CMR (Carcinogen, Mutagen, and Reprotoxic) [6]. Furthermore, isocyanates are derived from petrochemical materials, and thus, have negative environmental implications as well. Therefore, finding alternative routes to produce polyurethanes without the use of isocyanates is increasingly important as the global demand for polyurethanes continues to rise. Moreover, there is impetus towards using processes with a lower carbon footprint.

Through using non-toxic and renewable resources, researchers have been able to develop non-isocyanate polyurethanes (NIPU) in recent years. In fact, these NIPUs have even shown improved mechanical properties, thermal stability, chemical resistance, and lower permeability than conventional polyurethanes [7]. It is believed that the work of Groszos *et al.* [8] was the first to develop a method to prepare polyurethanes leading to the preparation of NIPUs [7, 9]. From this, four main routes towards synthesizing NIPUs have been developed since, which include

polycondensation, rearrangement, ring-opening polymerization, and polyaddition. Figure 1 summarizes these four routes below and shows that polyaddition is the only desirable route due to the absence of hazardous or toxic chemicals [9]. The polycondensation route involves 4 possible reactions, including polychloroformate + polyamine, polycarbamate + polyol, polycarbamoyl chloride + polyol, and finally polycarbonate + polyamine. The disadvantage with these reactions is that they all are linked to phosgene or its derivatives in some way. Furthermore, the synthesis of NIPUs via ring-opening polymerization with a cyclic carbamate is not only linked to phosgene as well, but it also involves other toxic chemicals such as aziridine [10]. Finally, synthesis via rearrangement is unfortunately also linked to toxic reactants such as acyl azide, carboxamide, and hydroxamic azide [9]. Therefore, perusing any of these routes would defeat the purpose of developing NIPUs altogether since the objective is to develop a less toxic and more eco-friendly polyurethane. Consequently, the final route of polyaddition is the most desirable option for NIPUs at this point.

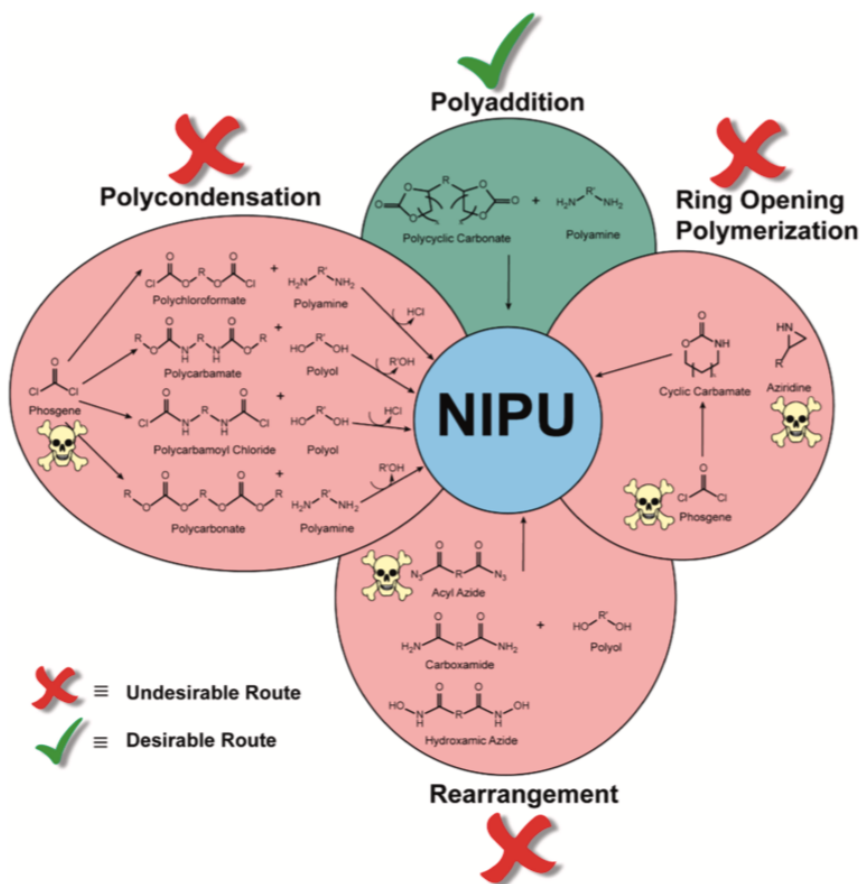
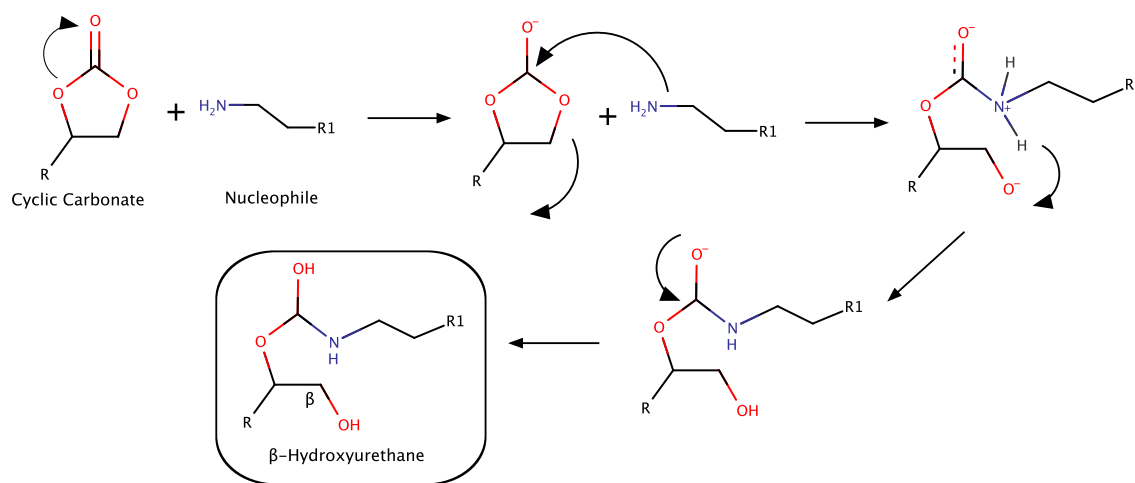


Figure 1: Main synthetic routes for developing NIPUs [9]. (Reprinted with permission from Elsevier)

1.1 Polyhydroxyurethanes

Polyaddition involves the reaction between polycyclic carbonate and polyamine resulting in the creation of a NIPU known as a polyhydroxyurethane (PHU). Polyamines can be obtained from commercially available products, thus making them a highly accessible and desirable reactant [7]. Polycyclic carbonates also are an excellent reactant due to their high solvency and boiling points, as well as their low toxicity and biodegradability [7]. Additionally, polycyclic carbonates are readily reactive with aliphatic and aromatic amines, alcohols, thiols, and carboxylic acids [11], making them a versatile reactant that can be tailored to give desired end products. It is important to note that polycyclic carbonates used in polyaddition reactions mentioned here are five-membered cyclic dicarbonates, as illustrated below in Scheme 1, since their synthesis does not require any phosgene derivatives as in the case of six- or seven-membered cyclic carbonates (CC) [6]. This reaction forms a linear β -poly(hydroxyurethane)s containing hydroxyl or hydroxy-methyl pendent groups [12].



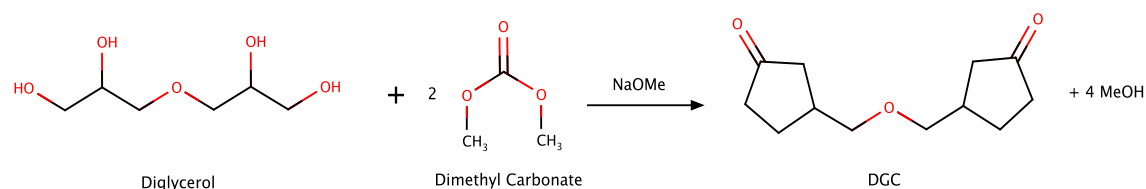
Scheme 1: Mechanism of polyaddition reaction of a five-membered cyclic carbonate with amine to form PHU (Adapted from Rossi de Aguiar *et al.* [12])

Conversely, the reaction given in Scheme 1 does have its weaknesses when compared to standard isocyanate-based polyurethanes. The five-membered CCs have low reactivity towards the polyamines as compared to the highly reactive isocyanates with polyols, giving lower polymerization rates for PHUs [9]. However, the formation of an intra-molecular hydrogen bond through the hydroxyl group at the β -carbon atom, adjacent to the urethane group, can contribute to higher water uptake and enhanced chemical resistance to organic solvents 1.5-2 times greater than

materials that have similar chemical structures without such bonds [4, 9, 12], PHUs can also be further modified due to the presence of the hydroxyl groups, allowing for a wide array of functionalized PHUs with tailored properties for specific applications [7]. Furthermore, NIPU synthesis is not as sensitive to moisture as traditional PUs are, which form urea and releases CO₂, resulting in a hardened and unusable product [12]. Overall, the low toxicity of CCs and polyamines, as well as the abundance of biodegradable, renewable and sustainable resources that can be converted into bio-based precursors for this reaction, make it a much more desirable route than conventional PU synthesis [9, 13].

In an effort to apply green chemistry principles in the plastics industry, there have been many publications and recent reviews on the replacement of CCs with renewable resources such as vegetable oils [13-16]. Other bio-based sources such as fatty acids, sugars, terpenes, glycerol, rosin gum, sorbitol, and cashew nut shells have all been investigated recently as well [12, 16]. These bio-based materials are of use in polymer synthesis due to their naturally occurring reactive sites, namely, ester groups and carbon-carbon double bonds, which are easily epoxidized and converted into CCs with the addition of CO₂ [12, 13]. Though there are several routes that can be taken when synthesizing PHUs, one of the more popular routes includes the use of diglycerol dicarbonate (DGC).

Glycerol is an abundant bio-based monomer that is a key side product of the biodiesel industry [17]. From this monomer, glycerol can be dimerized to form a tetrafunctional polyol known as diglycerol, which can then be converted into diglycerol dicarbonate through a reaction with a dialkyl carbonate, as shown below in **Scheme 2** [17].



Scheme 2: Synthesis of diglycerol dicarbonate from diglycerol and dimethyl carbonate. (Adapted from Velthoven *et al.* [17])

Most studies have focused on five- membered CC based PHUs, such as DGC, as bio-based routes to NIPUs [17-22], though there is some research into six- to eight- membered CC PHU synthesis as well [23-27]. These larger carbonate rings offer the benefit of being more reactive than their five-membered counterpart, however, suffer from poor stability in storage [18].

Interestingly, a recent paper by Tryznowski *et al.* [28] synthesized a bicyclic diglycerol dicarbonate bearing five-membered and six-membered CC groups from diglycerol and subsequently used this to synthesize a PHU. However, it was found that despite the different reactivities of the five- and six-membered CCs groups, the reaction of diglycerol dicarbonate was not selective and both groups reacted simultaneously. The studies on DGC-based PHUs overcame the low reactivity of 5-membered CCs through methods such as reactive extrusion [18], bulk conditions without the use of a catalyst [17], bulk conditions with the use of a catalyst [21], and high temperatures [20].

1.2 Objectives

Despite the growing interest in PHU development, there are some key challenges that hinder its ability to extend to industrial scale. Namely, the lower polymerization rates, as noted above, since it can be difficult to achieve linear polymers with high molecular weights. Additionally, PHUs tend to lack the mechanical and chemical properties that are required for specific applications. To overcome these limitations, inorganic/organic materials can be added with PHUs to create what is known as a Hybrid PHU (HPHU). Thus, this thesis will aim to give a review of the recent advances in HPHUs and how they have been used to overcome the limitations of PHU synthesis. Furthermore, this research will also aim to address the following three main objectives:

1. The synthesis of a specific and unique HPHU via the addition of polyhedral oligomeric silsesquioxane (POSS) to PHU prepolymers.
2. Investigate the effects of POSS in HPHU formulations as compared to PHU prepolymers and conventional PUs by thoroughly characterizing their structural, thermal, mechanical, and rheological properties.
3. Obtain final cross-linked HPHU films comparable to conventional PUs and suitable for sealant applications.

Materials and methods will also be given on how HPHUs in this work have been synthesized along with a detailed discussion on the results and future outlooks for HPHUs.

2.0 LITERATURE REVIEW

HPHUs have attracted a lot of interest as an attractive alternative to standard PUs. These hybrid materials can combine desired properties from different materials to create a product that is less toxic with enhanced mechanical properties. Therefore, HPHUs are an appealing and environmentally friendly alternative. There are three main routes in the synthesis of HPHUs, which includes the use of compounds with epoxy, siloxane, and acrylic functionalities. However, there are also some other noteworthy hybrids that have been investigated that either have a mix of these functionalities, or even use standard PUs in their formulation. This thesis explores the use of epoxy and siloxane methods and thus, this section will provide an overview of the recent and notable works done for these types of HPHUs.

2.1 Epoxy Hybrids

Epoxide materials are often used in the synthesis of HPHUs due to their reactivities with primary and secondary amine functional groups. Furthermore, the combination of epoxies with PHUs can give a material the chemical resistance of epoxies, with the good mechanical properties of PHUs. Within the epoxy hybrid categories, there are three possible synthesis routes to obtain these materials. First is reacting amine/carbonate terminated PHU prepolymers with an epoxy compound. Next is using a partially carbonated epoxide monomer and reacting it subsequently with polyamine to achieve a HPHU. Finally, the use of hydroxyurethane modifiers (HUM) with an epoxy compound will also give a HPHU material. These routes are all illustrated in Figure 2.

Though the research and development of HPHUs has increased in recent years, Rockicki was one of the first to investigate the chemistry between polyamines, CCs, and epoxides to obtain hybrid materials in the late 1980's [29, 30]. He first investigated modifying epoxy resins with carbon dioxide to obtain partially carbonated epoxide monomers and then cured this with triethylenetetramine (TETA) [29]. In a second study, Rockicki looked into crosslinking unmodified epoxy resins with curing agents containing β -hydroxyurethane linkages [30]. These curing agents were synthesized with polyamines and CCs. It was concluded that both methods lead to a comparable increase in the strength of the system and tended to shorten gel times. The first method falls in the category outlined in Figure 2A; crosslinking partially carbonated epoxide monomers, where the second method by Rockicki falls into the category illustrated in Figure 2B;

crosslinking PHU prepolymers. The following sections will further discuss the difference between these synthesis routes and provide a review of recent studies for each.

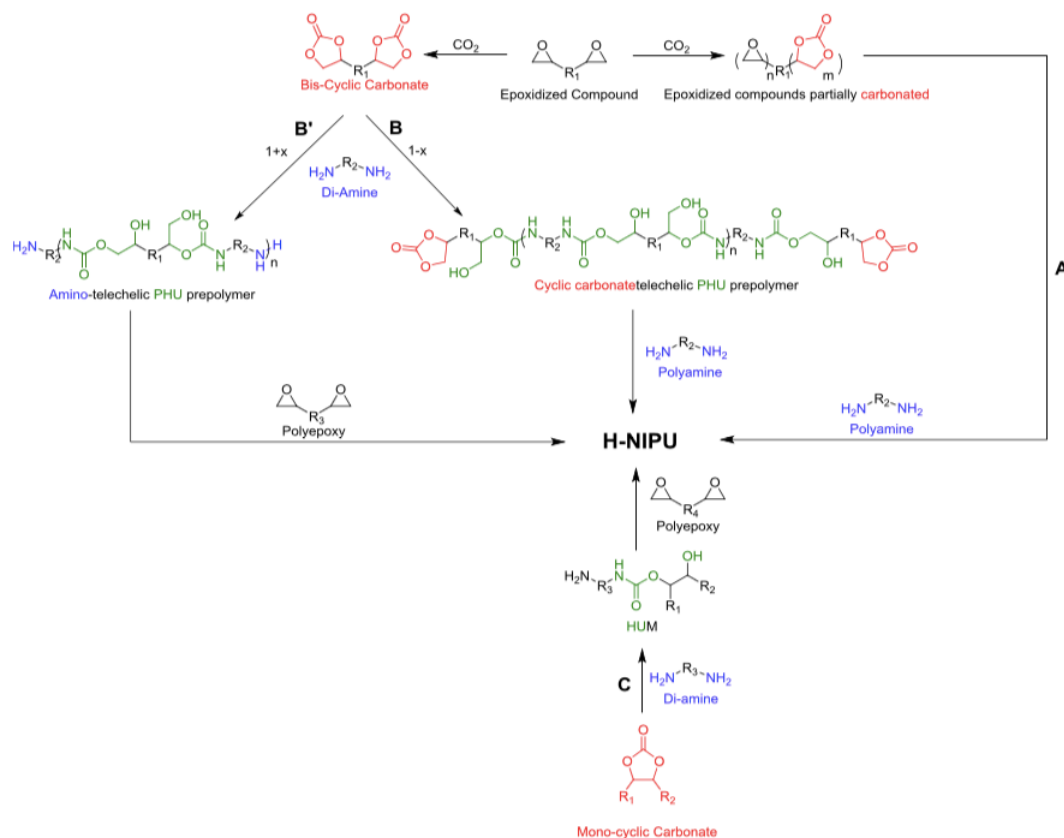


Figure 2: Methods to synthesize HPHUs from (A) crosslinking of partially carbonated epoxide monomers with a polyamine; (B) Crosslinking PHU prepolymers with carbonate end-groups, or (B') amine end-groups; (C) Crosslinking of hydroxyurethane modifiers (HUM) [3]. (Reprinted with permission from Elsevier)

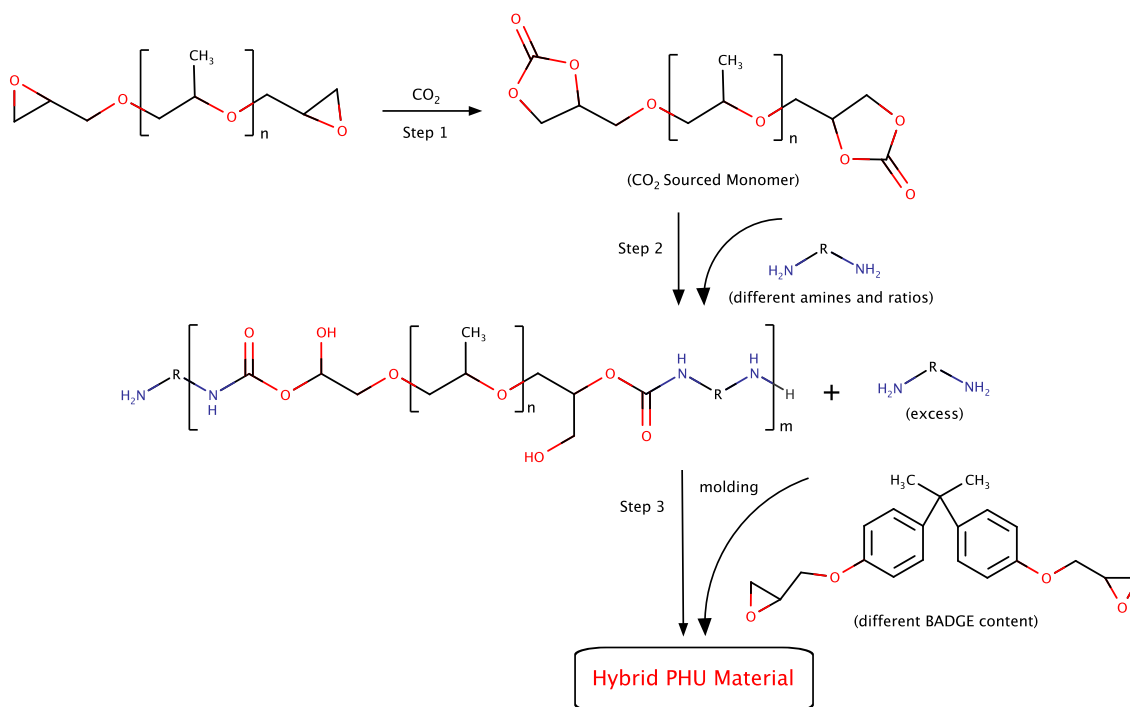
2.1.1 PHU Prepolymers

The PHU prepolymer method is one of the more popular routes towards obtaining hybrid polymers, owing to the reactivity of amine groups with other functionalities such as CCs and epoxides. Amine-functional (Figure 2B') or carbonate-functional (Figure 2B) PHU prepolymers are the two possibilities when synthesizing HPHUs with this method. With amine terminated prepolymers, an excess of diamine is used to obtain an amino-telechelic PHU prepolymer. From this, a poly-epoxy is added with the prepolymer that begins a ring-opening polymerization between the epoxy and amine compounds, thus forming a hybrid material. Conversely, a polyamine is added with carbonated functional prepolymers, which also causes a ring-opening polymerization; however, it is instead between CCs and amines.

One of the main advantages of this route is the ability to obtain materials with sequences of soft and hard segments, which is characteristic of standard PUs. Additionally, the high reactivity of epoxies to amines, as well as their ability to react with secondary amines, is an important factor in HPHU synthesis. This allows researchers to overcome the limitations in PHU synthesis and obtain more sophisticated materials.

Cornille *et al.* synthesized epoxyurethane polymers from isocyanate-free oligopolyhydroxyurethanes by using the amine-functional PHU prepolymer approach (Figure 2B') [31]. In this method, PHU prepolymers were synthesized with bis-cyclic-carbonates (poly(propylene oxide) oligomers PPO-380 and PPO-640) and varying excess (1.3, 2, 3.3, and 6.5) of ethylenediamine (EDA) at 60 °C for 12 h. Afterward, residual excess of EDA was removed by distillation under vacuum to obtain pure PHU oligomers. These PHUs were then further reacted at 50 °C for 12 h with three different multifunctional epoxy monomers, including bisphenol-A diglycidyl ether (BADGE), phloroglucinol tris-epoxy (PGTE), and diepoxy cardanol (NC-514). Overall, three epoxies were used in combination with five different PHU prepolymers. The study found that the glass transition temperature (T_g) was increased for the HPHUs, and they also exhibited good thermal properties when compared to standard PUs and other NIPUs. The main advantage of this method was noted by the ability to achieve PHU materials with a sequence of soft and hard segments similar to standard PUs.

In another study, Ke *et al.* also used an amine-functional prepolymerization method using CO₂ derived monomers and epoxies to synthesize HPHU materials [32]. The CO₂ sourced monomer was synthesized by a cycloaddition reaction between CO₂ and polypropylene glycol diglycidyl ether at 120 °C under 10 bar CO₂ as shown in **Scheme 3**. This resulted in a 5-membered CC (5CC), which was then further reacted with various diamines in excess at 90 °C for 4 h. Finally, the PHUs were combined with BADGE to obtain the hybrid materials. However, differing from the previous study, the excess amine was left in the system to increase the reactivity of the BADGE and improve the cross-linking of the final product. The study investigated the effect of amine ratio, type, and BADGE content on the properties of the resulting materials. They found that introducing BADGE as a chain extender and hard segment not only increased the crosslinking density, but also improved mechanical properties and thermal stability of the PHUs.



Scheme 3: CO_2 sourced monomer synthesized by a cycloaddition reaction from CO_2 and polypropylene glycol diglycidyl ether in the presence of an amberlyst catalyst. (Adapted from Ke *et al.* [32])

In a recent and in-depth study, Asemani *et al.* also took the amine functional PHU prepolymer approach [33]. However, in this study 16 CCs, 6 diamines, and 8 epoxies were combined in different ways and investigated. This resulted in 18 PHU prepolymers and 16 HPHUs overall. The goal of this study was to design coatings for advanced ambient temperature curing applications. Interestingly, they found that none of the final HPHUs alone met all of the performance criteria, which included flexibility tests, MEK double rubs, and tack-free time. This was attributed to the lower average functionality of the system, which leads to longer tack-free times, lower crosslinking density, and poor solvent and chemical resistance. To overcome this, two methods were used; the first was adding amines/amine adducts to the HPHU system, and the second was optimizing the functionality of the PHU prepolymers by using suitable CCs and amine blends. Coatings with outstanding performance features such as low temperature flexibility and resistance to chemicals were obtained. Furthermore, selected coatings containing PHUs with $M_n = 1480$ and 1:1.5 mol ratio of low-molecular-weight amine exceeded the performance of a conventional isocyanate-based PU. Results showed that the functional group content, backbone structure and molecular weight of the three components (CC, diamine, and epoxy) were key building blocks for the PHUs. Overall the final HPHU coatings displayed improved mechanical, physical, and chemical

properties. However, the thermal stability of the coatings is significantly inferior to that of conventional PU coatings. Despite this, the results are very promising for future development, and with the proper design, hybrid materials with properties comparable to standard PU coatings can be achieved.

More recently, Zhang *et al.* used waterborne amine-terminated PHUs with waterborne epoxy chain extenders to obtain a water-based HPHU [34]. Similar to the synthesis of standard waterborne PUs, waterborne HPHUs are prepared by dispersing a PHU prepolymer into water through neutralizing the incorporated internal dispersion monomer (IDM) on the PHU prepolymer chain. Waterborne polymers benefit from being more environmentally friendly than solvent-based polymers, and also offer a range of added applications in the coatings industry. The PHUs in this study were synthesized with DGC and fatty acid diamine (FDA). Overall, the hybrids with 50 wt% of FDA displayed two T_g s, similar to conventional PUs and indicative of phase separated microstructures. Additionally, the increasing the concentration of FDA as the soft segment also improved the thermal stability and mechanical strength. Though waterborne HPHU research is still in its infancy, this study shows promising first steps in the field. There are only a few other recent studies [35-37] as well as some reviews [38-40] so this is a field with a lot of potential for growth.

Herein, only studies using the amine terminated PHU prepolymer approach have been presented due to its popularity. This can be attributed to the wide range of amines that can be used for PHU synthesis, as well as the versatility of amino-functional compounds. However, Carré *et al.* used the CC-terminated prepolymer approach illustrated in Figure 2B [41]. To do this, a terephthalic bis-cyclic carbonate was synthesized from terephthalic acid and then further reacted with various long-chain diamines, including Jeffamine® D2000 and a dimer diamine (DDA). Using the CC in excess resulted in CC end-groups as well as some excess CC monomer in the PHU prepolymer. From here, short-chain diamines were added to the prepolymers, which included butanediamine (BDA) and m-xylylene diamine (mXDA), at 75 °C for 24 h and 7 days for the DDA and Jeffamine® based prepolymers, respectively. The study concluded that the molar ratio between the monomers, as well as side reactions, strongly impacted the thermal and mechanical properties of the resulting HPHUs. Specifically, HPHUs with high concentrations of diamine gave long soft chains that were susceptible to high elongation at break and low tensile strength. On the other hand, increasing the rigid building block content increased the overall tensile strength, but reduced the elongation at

break. Thus, the expected attractive properties of the standard PUs were missing. The resulting hybrid materials did give relatively good thermal and mechanical properties and possessed up to 76% biobased content. However, more research is needed to obtain a material with comparable or enhanced performance to conventional PUs through this method.

2.1.2 Carbonated Epoxide Monomers

The next approach in developing epoxy-based HPHUs involves the partial or full conversion of epoxy-functional monomers to CC functional ones. With partial conversion, only some of the epoxies are converted into CCs, resulting in one monomer with dual functionality. Another approach is to fully carbonate an epoxy-functional monomer and use both the carbonate functional and epoxy functional monomers, resulting in two monomers with different functionalities. The CC and epoxy functional groups can then further crosslink with amines to create a hybrid network. This reaction allows for both aminolysis of CCs and ring opening of epoxides, which leads to high conversion of monomers.

Figovsky was one of the earliest to investigate the partial carbonation approach of epoxy monomers to obtain hybrid materials and has filed several patents dating back to the late 1990's [42-44]. Among other earlier works for this method include Bürgel *et al.* [45, 46] and Rockicki *et al.* [29]. In each of these methods, an epoxy-functional monomer was partially carbonated to obtain one monomer with dual functionality and was then cured with an amine. Overall, a PHU crosslinked with polyepoxides afforded hybrids with better mechanical properties compared to similar PHUs.

More recently, Lambeth *et al.* used the full-carbonation method to achieve hybrid materials [47]. In this method, trimethylpropane triglycidyl ether (TMPTGE) was used as the epoxy monomer and was also carbonated and used as the CC monomer (TMPTGE-CC), giving two monomers with identical backbones but different functionalities (Figure 3). These monomers were also combined with 4,4'-methylenbis (cyclohexylamine) (PACM), which was chosen to achieve a high-modulus and polymers with a high T_g . Thus, all reactants were added together giving a one-step co-polymerization. This route was chosen due to the high boiling point of PACM at 330 °C, which would make complete removal difficult if a prepolymer approach was used. The ratio of TMPTGE to TMPTGE-CC was systematically varied to investigate how the ratio of PHU to epoxy in the polymer network impacts bulk mechanical properties and adhesive behavior. Overall, the materials performed as expected in terms of their swelling, thermal-mechanical, and tensile

properties based on the proposed network structure. In particular, the hybrid polymers with a 50/50 ratio of epoxy to CC performed very well as adhesives and were found to be amongst the highest reported values for adhesive properties. Increasing the CC content higher than this tended to decrease the T_g and increase the molecular weight between crosslinks (M_c), swelling index, and tensile yield stress. This was attributed to the significant hydrogen bonding observed in these formulations.

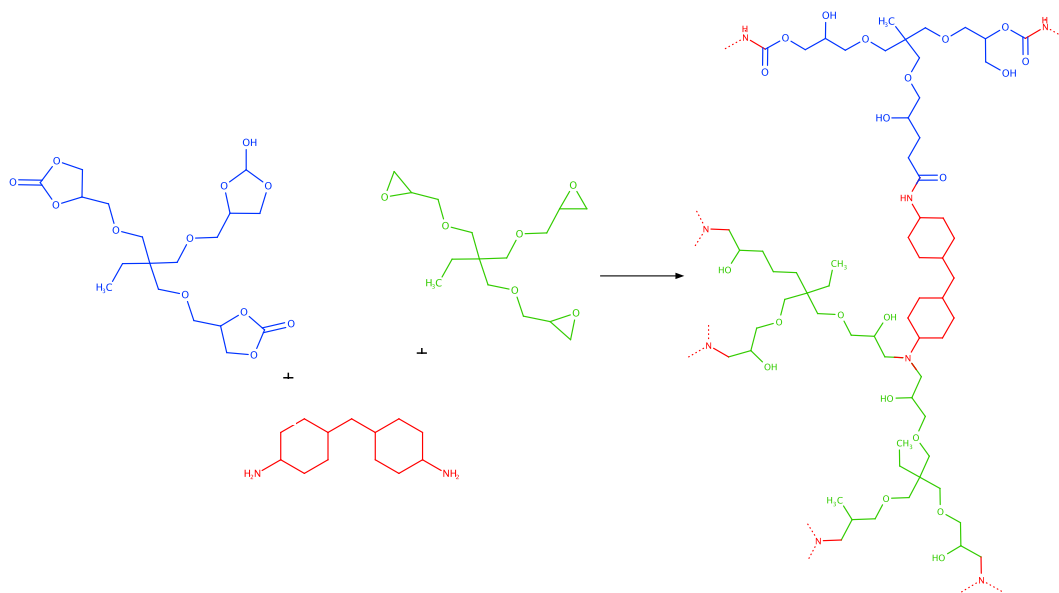
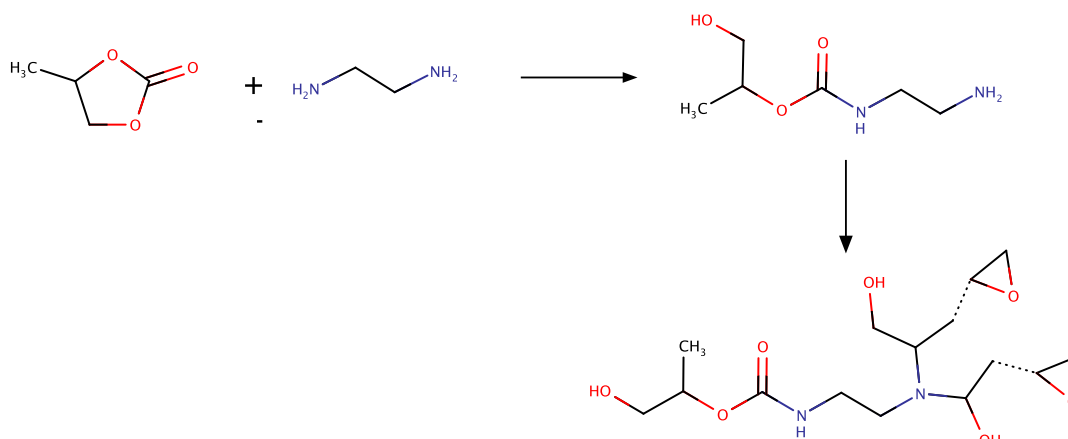


Figure 3: Synthesis of proposed epoxy hybrid network structure via total carbonation method (Adapted from Lambeth *et al.* [47])

2.1.3 Hydroxyurethane Modifiers

The final method for formulating epoxy-based hybrids is with the use of hydroxyurethane modifiers (HUM). This involves a two-step process, which first consists of reacting a difunctional amine and a monofunctional CC to obtain a HUM. The resulting unreacted amine can be further reacted in a second step with a polyepoxide, yielding a linear polymer with pendant hydroxyurethane functionality. This method was largely developed and patented by Figovsky *et al.*[48, 49] who synthesized several types of HUMs and also developed a concept for generating new multifunctional modifiers. The epoxy-amine system has been shown to give improved characteristics, such as curing time, mechanical properties, and water resistance over conventional polyepoxides. It is also important to note, that unlike the previous hybrid epoxy methods given above, the HUM and the polymer system are held together by a wide range of hydrogen bonds rather than direct covalent bonds.

More recently, in 2016, Wazarkar *et al.* synthesized HUMs through the reaction of propylene carbonate with ethylene diamine [50] - **Scheme 4**. This was then further reacted with commercial epoxies to achieve hybrid materials and then finally cured with several amines, such as isophorone diamine (IPDA), Jeffamine T-401, and diaminodiphenyl methane (DDM). They found that the addition of the urethane bonds and hydroxyl groups of the HUM in the backbone increases barrier and secondary mechanical properties, hydrophilicity, and adhesion, but the corrosion resistance was found to be somewhat less than that of conventional epoxies.



Scheme 4: Synthesized HUMs through the reaction of propylene carbonate with ethylene diamine. (Adapted from Wazarkar *et al.* [50])

2.2 Siloxane Hybrids

The next type of hybrid materials that can be formulated involve the use of siloxanes. These materials are interesting as siloxanes offer attractive properties such as mechanical strength, thermal stability, hydrophobicity, and flexibility. As with the epoxy method, there are also several routes in which siloxane-based materials can be incorporated into HPHUs. There is even a mixture of the two chemistries where an epoxy-functionalized siloxane can be used. Such materials include the use of polyhedral oligomeric silsesquioxane (POSS) and GLYMO. Additionally, silica-containing monomers with different functionalities along with sol gel routes can also be used to obtain siloxane hybrids. These methods will be further discussed in the following sections.

2.2.1 Silica Monomers

Silica monomers can be used for the synthesis of HPHUs, where several different functionalities can be manipulated. For example, silicas with amine, CC, and hydroxyl functionality can be used to form a hybrid network. Ecochard *et al.* recently synthesized multi-

functional linear and cyclic carbonate-siloxane monomers, which were then mixed with different amines to obtain HPHU thermosets [51]. The study synthesized four cyclic-carbonate-siloxane monomers via hydrosilylation and the CO₂ carbonation giving dangling CCs grafted on siloxane chains. These monomers offered high functionality and low viscosity, and when combined with oligomers, high conversions were also achieved. The monomers were cured with 1,3-cyclohexanedimethanamine (CBMA) and 2-methylpentane-1,5-diamine (DYTEKA). The structures of these siloxane monomers, along with the diamine cross-linkers are given in **Figure 4**. When comparing the two diamines used, there was found to be a +15 °C difference in the T_g for materials with CBMA, but no major differences in stiffness (E') were observed. The study also found that the difference in the functionality of the Si-3.5 and Si-6 monomers had a significant impact on the T_g and E' due to the higher cross-linking density given by the Si-6 monomer. The Eugenol monomer also contributed to a higher stiffness due to its aromatic ring. However, the monomer with the best performance in terms of T_g and E' was the D4-carbonate owing to its branched shape that gives high functionality and reactivity. Overall, the study highlighted the role functionality, the length and structure of the siloxane chain, and the choice of amine as a curing agent plays in HPHU synthesis.

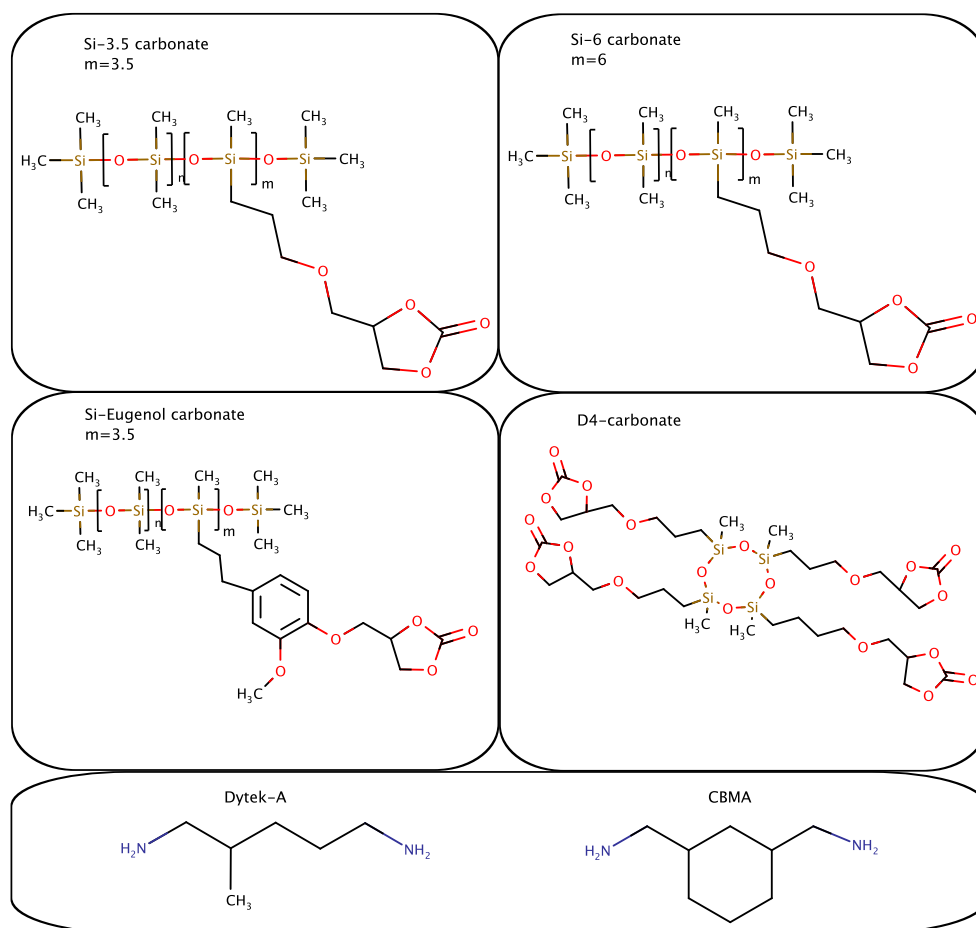


Figure 4: Structures of the four synthesized cyclic carbonate-siloxane monomers and two amine cross-linkers. (Adapted from Ecochard *et al.* [51])

In another study, Chen *et al.* focused on reprocessable PHUs using silica nanoparticles with different surface functionalities as reinforcing fillers [52]. Standard polymer networks are unable to be recycled for other applications due to the presence of permanent covalent cross-links. To overcome this and afford more recyclable PU materials, the researchers investigated adding three different types of silica nanoparticles. These include silica nanoparticles with hydroxyl functional groups (OH-silica), amine-terminated silica nanoparticles (NH-silica), and superhydrophobic silica nanoparticles (SHP-silica) which were made via proprietary modifications of surface hydroxyl groups. These silica nanoparticles were added into PHU networks and reprocessed 2-3 times. They found that the hydroxyl and amine groups of the OH-silica and NH-silica participate in side reactions, which negatively affect the cross-link density and mechanical properties of the PHUs compared to neat PHUs. However, when adding the SHP-silica to PHUs, significant improvement in mechanical properties was observed as well as a full recovery in cross-link density

after one reprocessing step. Thus, this study was able to successfully develop a reprocessable polymer network through the synthesis of a siloxane HPHU and serves as an important step towards recyclable polymers. Furthermore, it also highlights the importance of functional groups and how they can either be beneficial or detrimental to the properties of PHUs when reprocessed.

2.2.2 POSS-PHU Hybrids

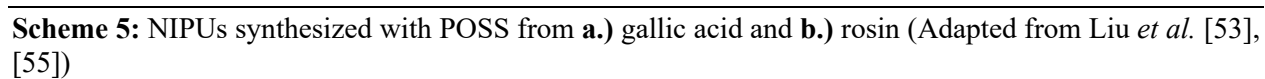
Polyhedral oligomeric silsequioxane (POSS) is a class of important inorganic-organic hybrid compounds that have attracted much interest due to their potential applications [53]. For polymers specifically, POSS has been shown to significantly improve mechanical properties, thermal stability, water tolerance, fire resistance, and dielectric properties [53]. Several recent reviews have examined the use of POSS in NIPU formulations specifically [52-56], and one examined the use of POSS with standard polyurethanes [57].

Liu *et al.* used POSS to modify gallic acid based epoxy resins [53], as well as rosin based epoxy resins [55] and is shown in **Scheme 5**. In the first study, a four-membered gallic acid-based epoxy resin was treated with CO₂ in the presence of a catalyst to obtain a tetra-carbonated material. The carbonate was then mixed with various diamines as well as epoxy functionalized POSS. This resulted in a network where one end of the diamine can react with a CC on the gallic acid-based monomer, and the other side can react with the epoxy group on the POSS. In a sense, the diamine is acting like a glue to bond everything together and obtain a final POSS modified hybrid resin. It was found that the addition of POSS strongly increased the water resistance of the NIPUs as increasing the POSS content decreased the water absorption. When high loads of POSS were added (20%) the pencil hardness was increased, but the adhesion was slightly inferior due to the increase of rigidity and brittleness of the material. The impact strength and flexibility, on the other hand, were not affected by the addition of POSS. Furthermore, POSS increased the thermal properties of the material as the T_g was significantly increased as well as the thermal degradation temperature (T_d). This was attributed to the increase of the crosslink density from the POSS.

In the second study, a very similar approach was used, however a rosin-based epoxy resin was used as the base material. Like the first study, the rosin resin was carbonated with CO₂ to obtain a three membered CC material and then various diamines and POSS were mixed in. However, this study also explores adding POSS in two different forms. First is the epoxy-functionalized POSS (same as the first study), and the second is in its carbonate-functionalized form. To get this second form, the epoxy-POSS is also treated with CO₂ in the presence of a catalyst. Overall, this results

in a network where the diamines again act like the glue to bond with the CCs on the rosin material and either the epoxy or CC groups of the POSS. Similar to the first study, the impact strength, flexibility, and adhesion were not significantly affected, while the water tolerance, pencil hardness and thermal stability were increased with increasing POSS content. When comparing the two different forms of POSS that were used, it was found that the materials containing the epoxy functionalized POSS provided higher water tolerance and pencil hardness, but lower T_g and T_d than the carbonate functional POSS when the same amount was added. This was attributed to the formation of urethane linkages and hydroxyl groups between the epoxy-POSS and amines.

Blattmann *et al.* [54] took a similar approach and formulated POSS/NIPU hybrid materials by first carbonating epoxy functionalized POSS with CO_2 . This study used two different forms of POSS, which was then mixed with three different CCs (based on glycerol, trimethylolpropane, and pentaerythritol) as shown in **Figure 5**. Finally, this mixture is cured with either hexamethylenediamine (HMDA) or isophoronediamine (IPDA). They found that adding 40% POSS in the coatings increased the Young's modulus from 31 to 1400 MPa (+4400%) without sacrificing elongation at break. Moreover, the scratch resistance was also improved with the incorporation of POSS as well as a reduction in the water uptake. However, the thermal stability was only marginally improved.



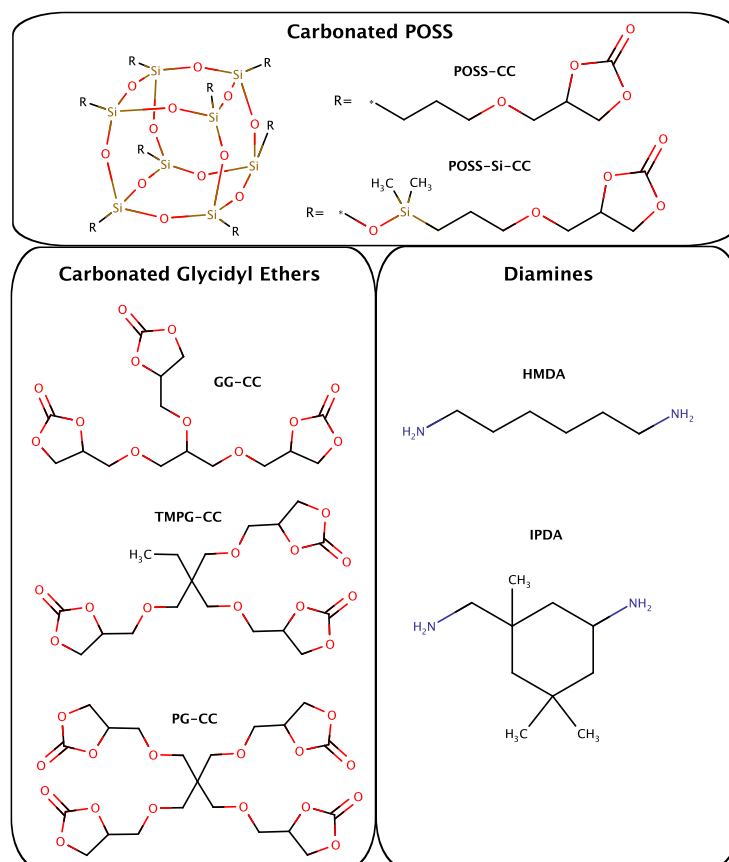


Figure 5: Chemical components of POSS containing NIPUs(Adapted from Blattmann *et al.*[54])

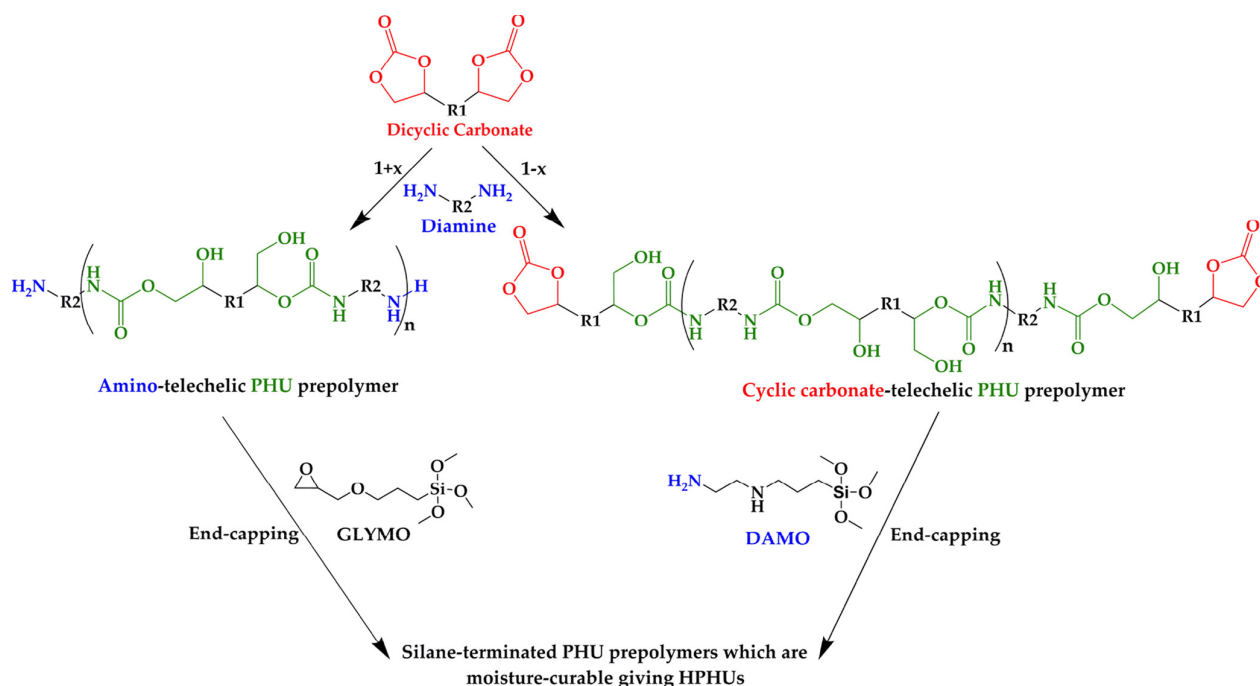
Finally, and most recently, Zhao *et al.* synthesized a POSS macromer bearing two six-membered CC (3,13-di(cyclic carbonate)) double decker silsesquioxane (DDSQ) and used this as a comonomer to obtain organic-inorganic PHUs with POSS cages in the main chains [56]. This study also uses the POSS in its CC functional form, however the synthesized DDSQ was added 4 hours after the diamine and CC, allowing formation of the polymeric material first. It was also found that the Young's modulus was increased for the NIPU, as well as developing shape memory properties and reprocessing properties at elevated temperatures. Overall, the incorporation of POSS into PHU materials has obvious benefits and can be used for a variety of purposes.

2.2.3 HPHUs via Sol-Gel Route

Finally, the third type of siloxane hybrid that can be synthesized is via a sol-gel route. In the previous methods described above, the siloxane moieties were added as monomers and found in the backbone of the polymer or within the polymer network. With the sol-gel route, silane groups are added on the ends of a polymer chain to cap it and give silane functionality. With respect to

this work, a sol-gel route is taken, however, polymer chains were capped with POSS, thus combining the two methods. This will be discussed in detail in subsequent sections.

Recently, Younes *et al.* synthesized partially bio-based PHUs with dicarbonates and various diamines [58]. In this work, DGC was first synthesized and added with different diamines to obtain PHU prepolymers, which were then end-capped with silane moisture-sensitive groups as shown in **Scheme 6**. Both amine-terminated and carbonate-terminated PHUs were synthesized. The carbonate-terminated PHUs were made from DGC and Jeffamine D-2000 (a poly(propylene glycol) (PPG) diamine) by reacting the DGC in excess. The amine-terminated PHUs were synthesized from DGC and poly(dimethylsiloxane) (PDMS) diamine (PDMS-5k-(NH₂)₂) with PDMS in excess. The appropriate moisture curable groups were added based on the functionality on the prepolymer, and this step did not require the use of a catalyst to achieve gel times from 3-7.5 hrs. The PDMS based PHU was let to cure in ambient conditions for one week and then an additional week immersed in water. The study found that the mechanical properties, tensile strength, and elongation at break improve with samples that were cured in water compared to those that were not. This, along with a high contact angle of 109°, indicate the hydrophobicity and water repellency of PDMS based HPHUs. Overall, this study successfully synthesized hybrid materials via a sol-gel route and highlighted the importance of amine selection as well as using the appropriate end-capper for curing reactions.



Scheme 6: PHU prepolymer synthesis and moisture-curing method for amine and carbonate end groups. From Younes *et al.* [58] <https://pubs.acs.org/doi/10.1021/acsomega.0c04689>. Note: further permissions related to this content should be directed to ACS.

Overall, the above methods give promising approaches to obtaining HPHUs that are comparable to conventional PUs. However, based on the current literature, more work needs to be done before these hybrid materials can fully, or even partially, replace PUs. Most studies have been able to achieve, and sometimes even exceed some of the desired properties, but never all of them. There are still some key drawbacks, such as cost, lower reactivities, and overall performance. More research is required to determine the right combination of materials to give all the desired properties. Nevertheless, NIPUs have been successfully developed from bio-based sources and the future is bright for this field as it moves into a more eco-conscience era.

3.0 MATERIALS AND METHODS

3.1 Materials

Diglycerol (DIG, $\geq 80\%$ α,α , impurities consist of mono-, α,β -di-, β,β -di-, and triglycerol) was obtained from Tokyo Chemical Industry (TCI). Dimethyl carbonate (DMC, $\geq 99\%$, anhydrous) and sodium methoxide (SOM, 95%, anhydrous powder) were purchased from Sigma-Aldrich and Acros, respectively. Ethyl acetate (EtOAc, certified grade), tetrahydrofuran (THF, HPCL grade), and dimethyl formamide (DMF, HPLC grade) were purchased from Fischer Chemical. Water purified by a reverse osmosis process (pure H_2O) was provided by the McGill Chemical Engineering Department. The diamines used in this work include Jeffamine D-2000, or PPG bis(2-aminopropyl ether) with $M_n = 2000$ g/mol (Aldrich), and Jeffamine D-4000 with $M_n = 4000$ g/mol. Aminopropyl Isobutyl POSS (A-POSS) (AM0265) and Nanosilica Dispersion Epoxy POSS (E-POSS) (EP4F09.01) were purchased from Hybrid Plastics. The catalyst 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) used in this work was provided by Sigma-Aldrich. 3-Isocyanatopropyl(trimethoxy)silane (IPTMS) and a proprietary tin-based catalyst were provided by ADFAST Corp. Deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$) and deuterated chloroform (CDCl_3) were provided from Sigma-Aldrich. DAMO or *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane was also purchased from Sigma-Aldrich. All the chemicals were used as received.

3.2 Experimental Methods

3.2.1 DGC Synthesis

The synthesis for DGC was optimized by Younes *et al.* [58]. First, 30.0 g of DIG is weighed and added into a two-neck round bottom flask equipped with a stir bar. Next, DMC is added at a 10:1 molar ratio of DMC:DIG (162.6 g). Finally, potassium carbonate is added as a catalyst at 0.5 wt% of the diglycerol (0.15 g). This mixture is then sealed with septa, added into an oil bath, and purged with nitrogen for 15 minutes. After this, the oil bath is heated to 75 °C and the mixture is allowed to react for 24 hours under magnetic stirring.

Once this reaction is complete, the mixture is filtered with a vacuum pump to remove any remaining catalyst, and the remaining liquid is left to strip under air for approximately 16 hours. After this time, the liquid volume is reduced to about 50 mL and 60 mL of refrigerated reverse osmosis (RO) water is added along with a stir bar and left to mix for 2 hours. During this time, any impurities are leached into the RO water, while the DGC is crystalized from the solution. This

mixture is then filtered again with a vacuum pump and the precipitated powder is collected and transferred into a beaker. The beaker is then charged with 30 mL of ethyl acetate and a stir bar and allowed to mix for an additional 30 minutes to remove any remaining impurities. Finally, this mixture is filtered again with a vacuum pump and the purified DGC powder is collected into a tin dish and topped with aluminium foil that was poked with small holes to allow any remaining volatiles to evaporate. This dish is then left to dry overnight in a vacuum oven to remove any remaining ethyl acetate. Once drying is complete, the final product is obtained. However, a small amount of DGC powder is first dissolved into DMSO-d₆ to run ¹H NMR to compare to a known pure sample of DGC to confirm that the synthesis was successful, and the product is clean from impurities. Once confirmed, the DGC powder is stored in glass vials to be used for subsequent prepolymer synthesis.

3.2.2 Prepolymer Synthesis

The prepolymer reaction was also optimized by Younes *et al.* [58]. DGC is mixed with an amine (Jeffamine D-2000 and Jeffamine D-4000 were used in this work) at different ratios depending on the functional groups that are desired. To obtain a prepolymer with amino functionality, an excess of Jeffamine is used at a 60:40 ratio. Conversely, to obtain a prepolymer with CC functionality, an excess of DGC is used at a 55:45 ratio. These mixtures are placed into a three-neck round-bottom flask reactor with a stir bar, sealed with septa, and then purged with nitrogen for 15 minutes. During this time, the reactor is submerged into an oil bath heated to 120 °C via a temperature controller and thermocouple and allowed to react for 24 and 28 hours for the Jeffamine D-2000 and Jeffamine D-4000 PHUs, respectively. After this, the resulting polymer is collected and stored at room temperature in glass vials for subsequent reactions. A schematic drawing of this reactor setup is given in **Figure 6**.

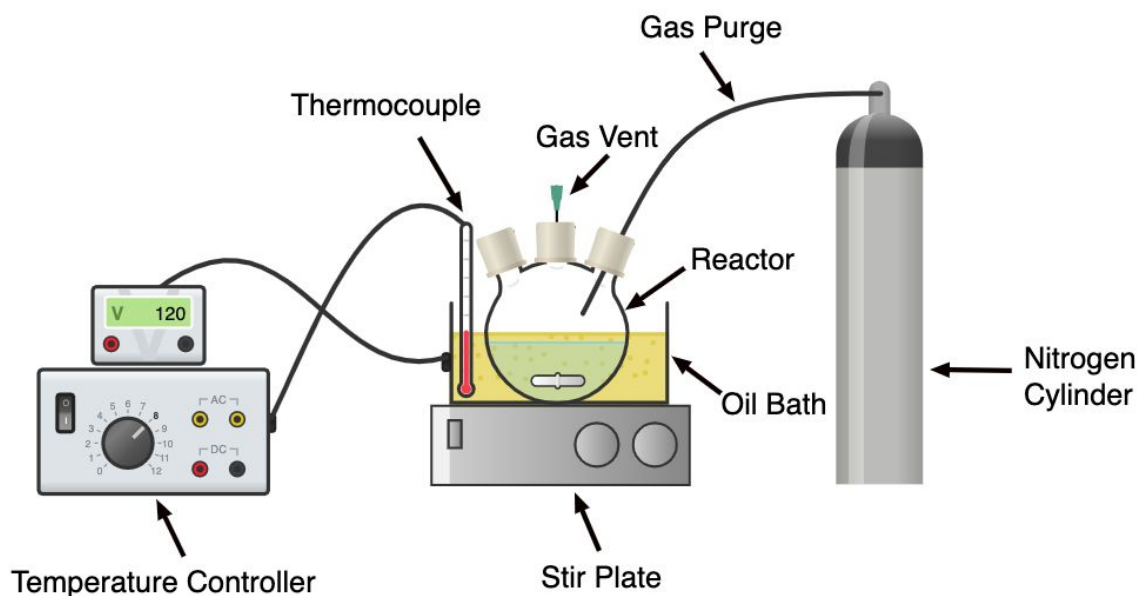


Figure 6: Schematic of reaction setup

3.2.3 Hybrid PHU Synthesis

The hybrid polymers were synthesized with the same reactor setup as given in **Figure 6**, however different conditions were used and will be discussed in the following sections.

3.2.3.1 Epoxy POSS

Epoxy POSS hybrid polymers were synthesized with prepolymers possessing amine functionality. The prepolymer was first synthesized with Jeffamine D-2000 in excess at a ratio of 60:40 with DGC and is referred to as PHU-1. Due to the high functionality of the E-POSS, different weight ratios from 1-20 wt% were investigated instead of stoichiometric amounts. The E-POSS was added into a reactor with PHU-1, heated from 60-100 °C and allowed to react for 24 hours. The E-POSS is a hard gel substance, therefore any unreacted POSS aggregated in the reactor and was removed easily from the polymer. The resulting polymer was then collected and stored in glass vials for subsequent analysis and reactions.

3.2.3.2 Amino POSS

To synthesize the amino POSS hybrid polymer, a prepolymer with CC end groups is required. Therefore, the prepolymer is first synthesized with DGC in excess at a 55:45 ratio with Jeffamine D-2000 and is referred to as DGC-PHU. After this, the DGC-PHU is weighed and added to reactor and a stoichiometric amount (2 mol of A-POSS for 1 mol of DGC-PHU) is also added. Since the reactivity of CCs to amines is slow, a small amount of catalyst is also added into the

reaction to promote the ring-opening polymerization of the CC with the amine. The catalyst used is 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) and is added at 0.5 mol%. This mixture was heated to 100 °C and allowed to react for 24 hours. After this time, the resulting HPHU was collected and stored in 20 mL glass vials where any unreacted A-POSS was left to settle out of the mixture. The A-POSS is a fine white powder, therefore the processes of settling took about 6-8 weeks before the top polymer could be collected for analysis and subsequent reactions. To aid in this process, a Thermo Scientific Sorvall Legend RT+ swing-bucket centrifuge was also used at a force of 3000 g for 1 hour. A second prepolymer was also synthesized with Jeffamine D-4000 with DGC in excess at a 55:45 ratio and is referred to as 4K-PHU. The exact same steps were taken to prepare this prepolymer, however it was allowed to react for 28 hours at 100 °C.

3.2.4 Silane Curing Synthesis

This end-capping synthesis was also completed with the same setup as given in **Figure 6**. Once the hybrid polymer is free from unreacted POSS, it is weighed and added into a reactor with varying amount of IPTMS. IPTMS is added stoichiometrically to react with the pendant hydroxyl groups in the backbone of the PHU.

Ratios of 10:1, 8:1, 5:1, 4:1, and 2:1 of IPTMS to HPHU were explored. The ratio of 10:1 was the maximum, where all hydroxyl groups would be reacted with an isocyanate group and 2:1 was the minimum where only two hydroxyl groups would be reacted. Once the ratio was selected, the appropriate amount of IPTMS was weighed and added to the reactor with the HPHU and allowed to react for 3 hours at 60 °C. After this time, the reaction was removed from heat and 0.02 wt% of a tin-based catalyst from ADFAST was mixed into the solution for 2 minutes. The mixture was then poured onto a Teflon sheet and spread into a thin film to allow the final hybrid material to cure in ambient conditions.

3.3 Characterization Methods

3.3.1 Size Exclusion Chromatography (SEC)

The PHU prepolymers and the HPHUs containing POSS were dissolved in HPLC grade THF at a concentration of 2.5 g/L in a 1-dram glass vial. The samples were measured on a Waters Breeze instrument with HPLC-grade THF as an eluent at a flow of 0.3 mL/min, powered by a Waters 1515 Isocratic HPLC pump. The instrument has three Waters Styragel HR columns (HR1 with a molecular weight measurement range of 10^2 to 5×10^3 g/mol, HR2 with a molecular weight

measurement range of 5×10^2 to 2×10^4 g/mol, and HR4 with a molecular weight measurement range of 5×10^3 to 6×10^5 g/mol), a (RI 2414) refractive index detector, and a guard column. An injection of 10 μ L of dissolved PHU or HPHU was taken by the apparatus and passed through the column, which was kept at a temperature of 40 °C. The samples were given 60 minutes to pass through the columns to capture the entire molecular weight distribution. The molecular weights were determined relative to PMMA calibration standards from Varian Inc. (ranging from 682 to 2,520,000 g/mol). The average number molecular weight (M_n), weight average molecular weight (M_w) and dispersity ($\bar{D}$) of the samples were reported using the instruments SEC software relative to the PMMA standards.

3.3.2 Fourier Transfer Infrared Spectroscopy (FTIR)

FTIR was performed on all PHU prepolymers and HPHUs as well as most cured samples. A Thermo Fisher Scientific Nicolet iS50 FTIR spectrometer equipped with a single bounce diamond attenuated transmission reflectance and a diamond DLaTGS detector was used. First, a background reading was performed on a clean diamond free from any sample to obtain an accurate baseline. The sample, either liquid or solid, was then placed on the diamond detector to fully cover it and was gently pressed to ensure adequate contact. A total of 32 scans were recorded for each sample over the range 4000-400 cm^{-1} . The results were plotted with respect to % transmittance and analyzed with Thermo Fisher Scientific Omnic software.

3.3.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR was performed on both the PHU prepolymers and the HPHU materials. Approximately 5 mg of polymer was dissolved in 2 mL of CDCl_3 and 0.5 mL of this solution was transferred into an NMR tube. DGC was also analyzed via NMR; however, it was dissolved into a solution of $\text{DMSO-}d_6$. All samples were run with ^1H NMR and only a select few HPHU samples were run with ^{29}Si NMR to confirm the presence of POSS in the samples.

3.3.3.1 ^1H NMR

Proton NMR experiments were conducted on a Bruker 500 MHz NMR Spectrometer in 1D using 16 scans. The analysis was completed at room temperature with a zg30 pulse sequence. The resulting spectra was analyzed and interpreted using Mestrelab MNova software.

3.3.3.2 ^{29}Si NMR

^{29}Si NMR experiments were also conducted on a Bruker 500 MHz NMR Spectrometer using a heteronuclear multiple bond correlation (HMBC) between ^1H - ^{29}Si . The signal first excites on ^1H , and then transfers the signal to ^{29}Si to detect ^{29}Si in the vertical (indirect or f1) dimension of a 2D experiment, and then transfer back to ^1H for detection in the horizontal (direct or f2) dimension. The resulting spectra was analyzed and interpreted using Mestrelab MNova software.

3.3.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is used to determine the thermal degradation of the PHU pre polymers and A-POSS HPHUs to discern any differences. A TA Instruments Discovery 5500 thermogravimetric analysis machine was used. First, a small platinum pan is cleaned with a blow torch to remove any residue from previous samples, then weighed and tared. Next, approximately 5 mg of sample is added into the pan and weighed by the machine to get an exact measurement. Finally, the sample is loaded into the furnace chamber where it is heated from ambient temperature to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere. The resulting thermal degradation plot was analyzed with TA Instruments Trios software in which the onset degradation temperature ($T_{d,\text{onset}}$) and 10% degradation temperature ($T_{d,10\%}$) were calculated.

3.3.5 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was used to determine the glass transition temperature (T_g) of the PHU prepolymers and A-POSS HPHUs. A TA Instruments Discovery 2500 DSC machine was used. A standard hermetic aluminium pan is first weighed and tared, then 5-10 mg of a sample is added. The pan is then sealed with a top using a press machine and weighed again to determine the sample weight. The pan is loaded into the machine and analyzed in a nitrogen environment. A heat-cool-heat experiment is performed where the machine heats the sample to 120 °C at a rate of 10 °C/min, then cools to -90 °C, and finally heats it again to 120 °C. The resulting plot was analyzed with TA Instruments Trios software and the T_g was calculated from the second heating ramp.

3.3.6 Gel Content

Gel content was only performed on cured samples. Three square samples, approximately 10x10 cm were cut from a cured film and each placed into pre-weighed 20 mL vials. The vials were then weighed again to determine the initial weight of the cured samples. Finally, 10 mL of THF was

added to the vials to submerge the samples, which were then capped and left undisturbed for one week to soak. After this time, the samples were filtered, and the remaining solid sample was immediately weighed to determine the swollen mass. The samples were then transferred back to their respective 20 mL vials and topped with aluminium foil perforated with small holes. The vials were then placed into a Fisher Scientific Isotemp® vacuum oven model 281A connected to a Welch® 8917 vacuum pump. The pressure inside the oven reaches approximately -30" gauge and the samples were left to dry at room temperature overnight for 15 hours. Once dry, the samples were removed from the oven and weighed again to determine the dry mass of the samples. The average of the three samples was taken and reported as a mean value to give a more accurate value for the gel content. The gel content, and swelling index are given below in equations 1 and 2, respectively.

$$(1) \quad GC(\%) = \left(\frac{W_f}{W_i} \right) \times 100$$

$$(2) \quad SI(\%) = \left(\frac{W_s - W_i}{W_i} \right) \times 100$$

Where W_f is the final weight of the dried sample, W_i is the initial weight of the sample, and W_s is the weight of the swollen sample.

3.3.7 Water and Toluene Swelling

Water and toluene swelling was also only performed on cured samples. Three square samples, approximately 10x10 cm were cut from a cured film and each placed into pre-weighed 20 mL vials. The vials were then weighed again to determine the initial weight of the cured samples. Finally, 10 mL of RO water or toluene was added to the vials to submerge the samples, which were then capped and left undisturbed for one week to soak. After this time, the samples were filtered, and the remaining solid sample was immediately weighed to determine the swollen/final mass. The average of the three samples was taken and reported as a mean value to give a more accurate value for the water or toluene swelling. The water and toluene absorption (WA%) values were calculated from equation 3.

$$(3) \quad WA(\%) = \left(\frac{W_f - W_i}{W_i} \right) \times 100$$

3.3.8 Rheology

Rheology experiments were performed on an Anton PAAR MCR 302 modular compact rheometer with a CTD 450 furnace. Air flow of 1400 Nl/h was used for shaft cooling along with 850 Nl/h of air or nitrogen, depending on the experiment, to the furnace. The Anton PAAR PP25 25 mm diameter parallel plate sensor is used for all steady shear viscosity and parallel curing tests. The results were analyzed with Rheocompass software connected to the rheometer.

3.3.8.1 Steady Shear Viscosity Test

1 mL of a polymer sample is placed onto the bottom 25 mm diameter parallel plate so that it is fully covered. The top PP25 plate is then lowered to give a 1 mm gap between the plates for the sample to fill and any excess from the sides is trimmed. All experiments are performed at ambient conditions. The shear stress is measured at different shear rates from 0.1 to 10 s⁻¹ with 21 readings over 3 min. The resulting viscosity curve is analyzed and an average viscosity (η) is reported.

3.3.8.2 Parallel Plate Curing

Once completing a curing experiment, as outlined in section 3.2.4, 1 mL of the polymer is immediately transferred to the bottom 25 mm diameter parallel plate of the rheometer so that it is fully covered. The top PP25 plate is then lowered to give a 1 mm gap between the plates for the sample to fill and any excess from the sides is trimmed. All tests were performed at ambient conditions with the furnace doors open to expose the sample to air during the experiments. The experiments were performed at a frequency of 1 Hz and a strain of 1 % with a humidity range from 25-60%. The instrument performed shear rheological measurement every 10 seconds recording the storage modulus (G') and loss modulus (G'') until the gel time was observed, which is when the curves intersect. Depending on the experiment, the samples were allowed to cure from 24-48 hours.

3.3.9 Tensile Testing

Tensile testing is only performed on cured samples as described in section 3.2.4. Once the sample is fully cured (~1 week) on a Teflon sheet, 3-5 dog bone shaped bars are cut out of the film with a punch mould. The dimensions and shape of the bars are given in **Figure 7**. The bars are then carefully measured with digital calipers for their thickness, length, and width of the middle section to an accuracy of 0.01 mm. The samples are analyzed at ambient conditions with a Shimadzu EZTest Tensile Testing machine using WinAGS Lite software. Once the measurements

are complete and entered in the software, the sample is clamped into the machine and pulled at a speed of 10 mm/min. The resulting stress strain curve is produced, in which the Young's modulus (E), elongation at break (EB%), and tensile strength (σ_{max}) can be calculated. The results are averaged over at least three repeated film samples of one cured polymer and reported with error bars indicating the minimum and maximum values recorded.

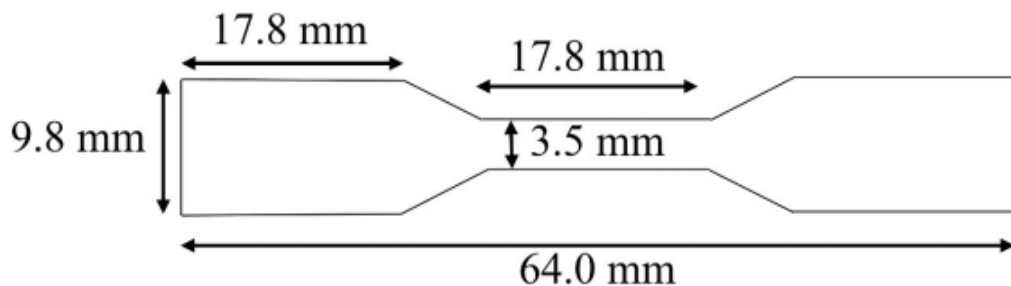


Figure 7: Tensile testing dog bone dimensions

3.3.10 Water Contact Angle Measurements

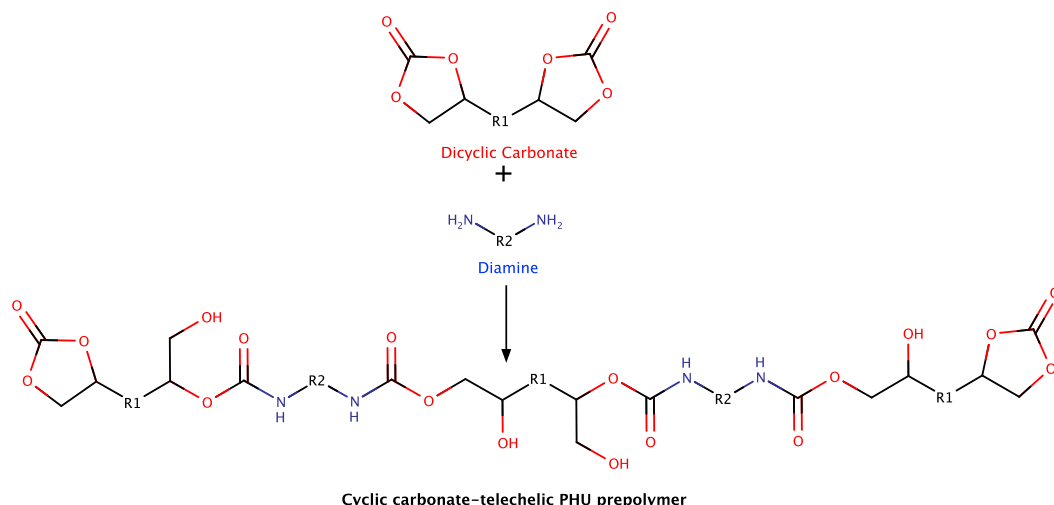
Water contact angle measurements were performed on an OCA 150 apparatus (DataPhysics Instruments GmbH) with a sessile drop configuration that deposited 5 μL droplet of Milli-Q water at a rate of 0.5 $\mu\text{L/s}$ with a 0.5 mL GASTIGHT #1750 syringe. SCA20 software was used to determine the mean contact angle from five repeated measurements taken at different points on the sample.

4.0 RESULTS AND DISCUSSION

The work for this thesis can be categorized into three main segments: the synthesis of prepolymer PHUs, the addition of POSS to synthesize HPHUs, and finally moisture curing reactions to obtain final cured HPHU films. As mentioned in section 3.2.2, Younes *et al.* [58] optimized the reaction for both the monomer synthesis of DGC, as well as the PHU prepolymer. These conditions were taken and used to form CC functional PHU prepolymers that served as a benchmark for the work as well as parent materials for subsequent HPHU reactions. Thus, the focus and much of the work for this study was put into the synthesis of HPHUs with POSS. Several different characterization methods were used to confirm and quantify the addition of POSS into the polymer network. Subsequent curing reactions were also optimized and thoroughly characterized to determine the overall properties of the final HPHU films, all of which will be discussed in detail in the following sections.

4.1 Prepolymer Synthesis and Characterization

Two different PHU prepolymers were synthesized in this work. The first was with the diamine Jeffamine D-2000 ($M_n = 2000$ g/mol) with the dicarbonate DGC in excess. The next was synthesized with Jeffamine D-4000 ($M_n = 4000$ g/mol), also with DGC in excess. **Scheme 7** gives the general synthesis route to produce these cyclic carbonate-telechelic PHU prepolymers. CC-terminated prepolymers were used instead of amine terminated as CC groups were needed to react with the amino-functional POSS in following HPHU reactions. The Jeffamine D-2000 based PHUs were previously optimized with conditions at 120 °C for 24 hours. However, the Jeffamine D-4000 based PHUs were not previously synthesized and therefore the optimal conditions needed to be worked out. Since the Jeffamine D-4000 is a longer chain diamine, the PHU synthesis reaction was left to react for an additional 4 hours to give a total of 28 hours at 120 °C. This resulted in a PHU that had a similar molecular weight, but with a longer soft segment to give different properties than the Jeffamine D-2000-based PHU. To characterize these polymers, GPC, FTIR, and ^1H NMR testing methods were used.



Scheme 7: CC-terminated PHU prepolymer synthesis

4.1.1 GPC Results

GPC was first used to determine the molecular weights of the PHU prepolymers. This elucidated the average length of the polymer chains and was also necessary to perform subsequent stoichiometric calculations for the HPHU synthesis. The average molecular number weights (M_n) given in **Table 1** are taken from the GPC and are relative to PMMA linear standards. To obtain the absolute molecular weight the following calculations were performed:

- The average number molecular weight, M_n , of DGC-PHU-11 from GPC data is:

$$M_n = 5,900 \text{ g/mol}$$

- The average number molecular weight of Jeffamine D-2000 from GPC data is:

$$M_n = 1,800 \text{ g/mol}$$

- Dividing the molecular weight of DGC-PHU-11 by Jeffamine D-2000 gives the number of diamine molecules in the prepolymer chain:

$$5,900 / 1,800 = 3.28 \approx 3$$

- Thus, each PHU chain has 3 Jeffamine units, which are separated and end-capped by DGC (as further confirmed by FTIR and ^1H NMR), giving 4 DGC units. Knowing the absolute molecular weight of DGC is 218 g/mol and Jeffamine D-2000 is 2000 g/mol, the absolute average number molecular weight of DGC-PHU-11 is:

$$M_n^{\text{absolute}} = (3 \times 2000) + (4 \times 218) = 6,872 \text{ g/mol}$$

- Similarly, for determining the absolute M_n for the 4K-PHU:

$$M_n^{absolute} = (2 \times 4000) + (3 \times 218) = 8,654 \text{ g/mol}$$

From these results, all PHU prepolymers that were synthesized were oligomers with a maximum of 3 diamine units. Though oligomers are considered small chain polymers, the Jeffamine units are in fact long chain polymers themselves, and thus provide the PHU long soft segments that are characteristic of conventional PUs.

Table 1: Average and absolute molecular weights of the PHU prepolymers

Sample	Amine	Time (h)	Temp (°C)	Average M_n (g/mol)	Dispersity ($\bar{D}$)	Absolute M_n (g/mol)
Jeffamine® D-2000	-	-	-	1,800	1.20	2,000
Jeffamine® D-4000	-	-	-	3,700	1.38	4,000
DGC-PHU-11	Jeffamine® D-2000	24	120	5,900	1.64	6,872
DGC-PHU-12	Jeffamine® D-2000	24	120	5,100	1.92	6,872
DGC-PHU-13	Jeffamine® D-2000	24	120	5,900	2.15	6,872
DGC-PHU-14	Jeffamine® D-2000	24	120	6,400	2.05	6,872
4K-PHU	Jeffamine® D-4000	28	120	5,900	1.99	8,654

4.1.2 FTIR Results

FTIR is a useful tool in determining functional groups of molecules and was instrumental in the characterization of both the PHU prepolymers and final HPHUs. **Figure 8** shows the labelled FTIR spectra for DGC-PHU-11. A C=O peak appears at 1800 cm^{-1} and is indicative of the CC groups on the ends of the polymer. This peak was confirmed to be the CC peak on the end of the polymer and not unreacted DGC as purification in toluene and hexane was completed to remove any impurities from the prepolymer. The purified sample was also subjected to FTIR analysis and the C=O peak at 1800 cm^{-1} remained the same. The peak to the right of this, at 1720 cm^{-1} , corresponds to the urethane bonds that are formed between the CC and amine groups of the DGC and Jeffamine monomers. This spectrum not only confirms the successful synthesis of a NIPU with the urethane peak, but also illustrates that a CC-terminated PHU prepolymer was achieved.

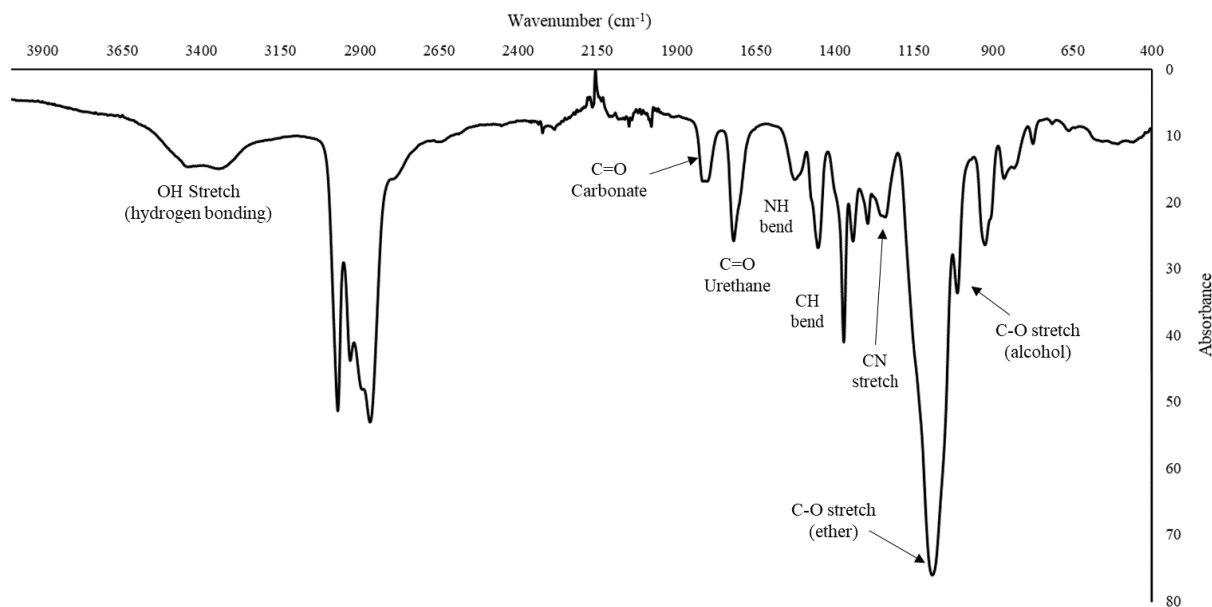


Figure 8: FTIR spectra of DGC-PHU-11 prepolymer with labelled peaks.

4.1.3 ^1H NMR Results

Finally, ^1H NMR was used to obtain information about the molecular structure beyond just the functional groups. This was used to further confirm the successful synthesis of the PHU prepolymers. Predicted ^1H NMR spectra were utilized to aid in the deconvolution of peaks as well as provide a basis for the real ^1H NMR spectra.

The predicted ^1H NMR spectrum for Jeffamine D-2000 is given in **Figure 9**. In this figure, group *b* is the most prevalent peak, which is due to the repeating CH_3 group. It is also upfield and split into a doublet, along with group *a*, since they are both away from electronegative atoms and their neighbouring bonds only contain one proton. Group *e*, on the other hand, is the most downfield and split into multiple peaks, which is attributed to the fact that these protons are close to an electronegative oxygen atom as well as within the repeating units. From this predicted ^1H NMR spectrum, the most prevalent peaks are from 1-1.5 ppm and 3.5-4.5 ppm and therefore it is expected to observe similar peaks in the Jeffamine based PHU and HPHU.

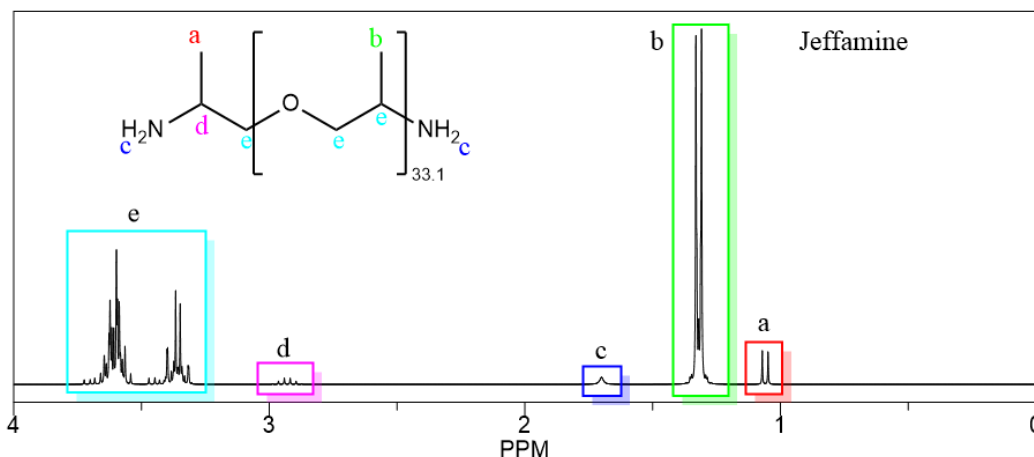


Figure 9: Predicted ^1H NMR spectrum of Jeffamine D-2000

The predicted NMR spectrum of the PHU synthesized from DGC and Jeffamine is shown in **Figure 10**. This NMR spectrum gives several peaks as there are plenty of interchanging oxygen and nitrogen atoms, which are very electronegative and cause a variety of chemical shifts. Additionally, this prediction gives a good basis for what to expect on a real NMR spectrum, however due to its polymeric nature, key differences should be expected. For example, in this prediction group *c* is small compared to group *a*, which is due to group *c* is being considered as one carbon (chain) with two hydrogens, where group *a* is at the end of a chain and has three hydrogens. In reality, group *c* will consist of a chain of carbons with several hydrogens attached and thus be larger. Group *a*, on the other hand, will connect to other PHUs to create the polymer, and therefore will only have two hydrogens attached making it smaller. To illustrate these differences, **Figure 11** shows a real NMR spectrum for the DGC-Jeffamine PHU. It is also important to note that group *c*, or the carbon chain R^1 , represents the repeating units in Jeffamine D-2000.

The predicted and real ^1H NMR spectra given in **Figure 10** and **Figure 11** give very similar results, apart from group *c*, which is expected. Group *c* represents the repeating unit in Jeffamine D-2000 (shown in **Figure 9**), which contains an oxygen atom and thus, group *c* moves downfield and appears in the peak with *b* and *f*. Furthermore, the main peaks appear in the ranges of 1-1.5 ppm and 3-4 ppm, confirming that the PHU was successfully synthesized.

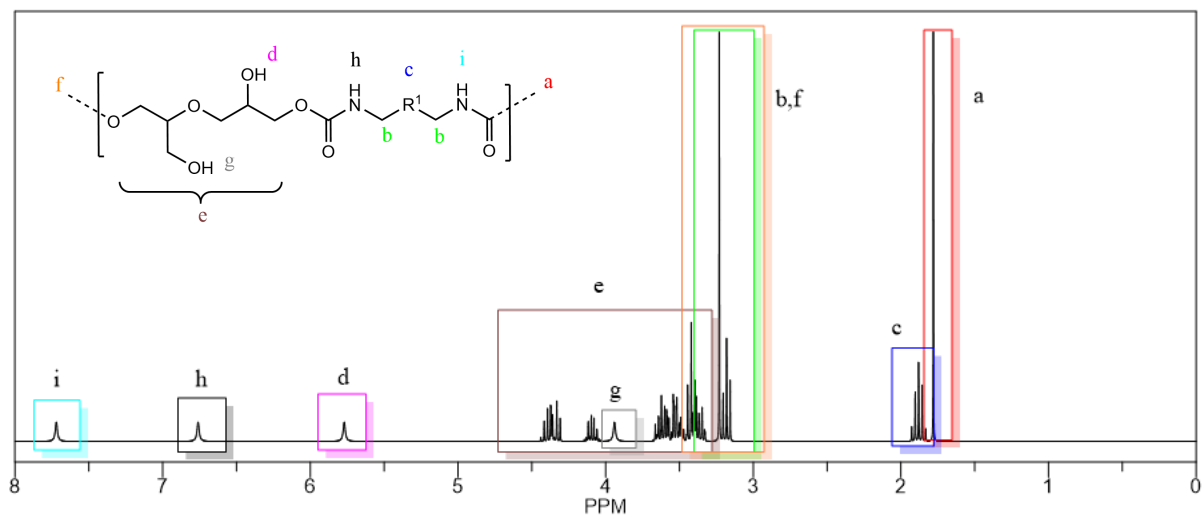


Figure 10: Predicted ^1H NMR spectrum of a PHU molecule

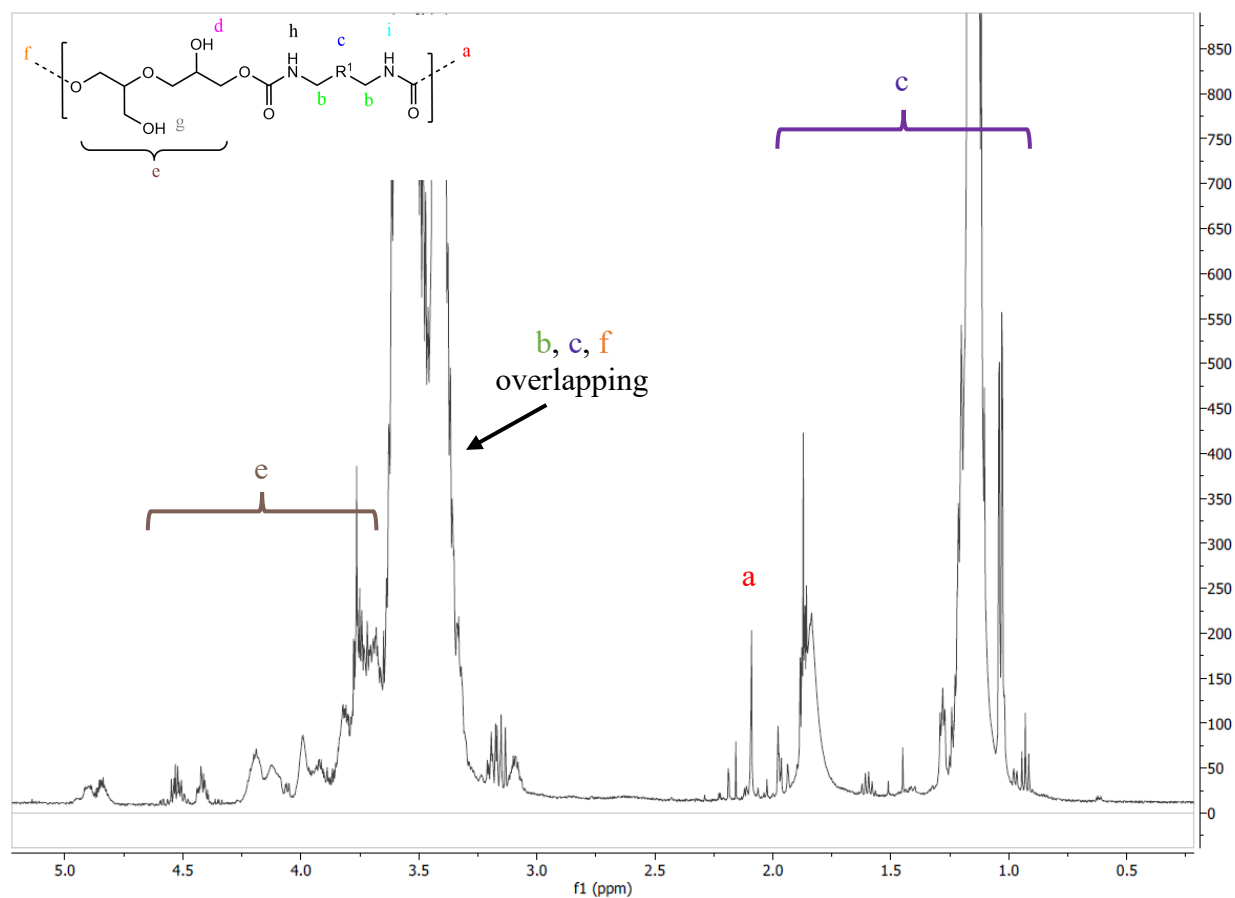
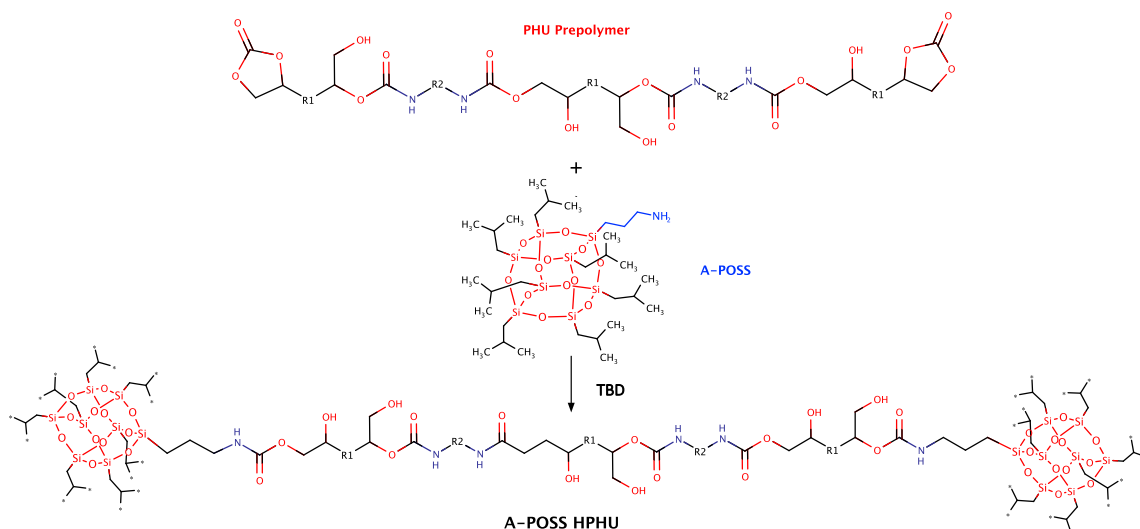


Figure 11: ^1H NMR Spectrum of DGC-Jeffamine prepolymer

4.2 HPHU Synthesis and Characterization

Once the PHU prepolymers were synthesized and fully characterized, work on synthesizing the HPHUs could begin. This comprised the bulk of the work for this thesis and careful attention was directed towards ensuring POSS was covalently bonded to the polymer and not just mixed as an additive. The reaction conditions as well as the type of POSS used were also carefully investigated to be able to obtain a final POSS modified HPHU. At the start of this work, an 8-membered epoxy functionalized POSS (E-POSS) was initially explored and reacted with the amine-terminated PHU prepolymer. This reaction proved too difficult to control and characterize due to the 8 epoxy groups on the POSS, and therefore a monofunctional amino POSS (A-POSS) was then studied instead. The A-POSS was mixed with the CC terminated PHU prepolymer and was essentially used as an end-capping agent for the polymer as shown in **Scheme 8**.



Scheme 8: Synthesis of HPHU from PHU prepolymer and A-POSS

There were three methods or attempts that were investigated for this synthesis. The first was mixing the A-POSS with the amine-terminated PHU prepolymer. This was unsuccessful as the amine end groups of the polymer were incompatible with the amine functionality of the POSS. Next, the synthesis of the A-POSS HPHU was attempted with the CC terminated PHU prepolymer, but without the use of a catalyst, which also led to unsuccessful results. This is attributed to the lower reactivity of CCs to amine [11] as well as the bulky nature of POSS, which can make it more difficult for this reaction to occur. Finally, the third method to obtain A-POSS HPHUs was with the CC terminated PHU prepolymer and TBD as a catalyst. This method was ultimately successful,

however several trials were required to determine the optimal amount of TBD required as too much caused unwanted side reactions, but too little resulted in no reaction. This will be further discussed in the following characterization sections in addition to the final formulation that successfully incorporated the A-POSS into the PHU prepolymers.

The three methods mentioned above all used Jeffamine D-2000 as the diamine for the PHU prepolymer. The third and successful method resulted in A-POSS modified HPHUs with Jeffamine D-2000 in the backbone with the help of TBD as a catalyst. Taking the reaction conditions found from this method, this synthesis was then slightly altered to create a different set of HPHUs for comparison. Specifically, PHU prepolymers were synthesized from Jeffamine D-4000 and then further functionalized with A-POSS. Almost the same reaction conditions were used for this synthesis, however longer reaction times were required due to the longer chain diamine used. This resulted in HPHUs with larger soft segments that offered different properties. Overall, these two HPHUs were fully investigated and characterized and provided insight on how diamine selection can affect the final properties.

4.2.1 FTIR Results

The most effective characterization method for the HPHU synthesis was FTIR. FTIR helps to determine functional groups, and since this synthesis involves modifying functional groups, changes in the spectra were easily detected. As shown in **Figure 8** above, the CC end groups and the urethane peaks appear around 1800 cm^{-1} and 1720 cm^{-1} , respectively. These were the main peaks that were investigated during FTIR analysis as the CC peaks are expected to diminish while the urethane peak increases. This occurs because as the CC end groups of the PHU prepolymer react, they turn from CC groups to urethane bonds, which will reflect in the FTIR spectra. **Table 2** summarizes the initial HPHU reactions that were carried out and shows the amount of TBD catalyst that was used. Additionally, **Figure 12** gives the zoomed in FTIR spectrums for these reactions from 1500 cm^{-1} to 1950 cm^{-1} . In the figure, the PHU prepolymer (named DGC-PHU-4 and shown in blue) shows the CC peak of the end groups at 1800 cm^{-1} and the urethane peak at 1720 cm^{-1} . However, HPHU-A3.1, A3.3, A3.4, and A3.7 are all showing a decrease in the urethane peak and a new peak from 1650 cm^{-1} to 1675 cm^{-1} , which is indicative of urea formation [21]. The formation of urea is an unwanted side reaction as it is desired to keep the urethane linkage intact to form HPHUs. As shown in **Table 2**, these reactions use TBD amounts from 2.5 to 20 mol% at different times and temperatures. These TBD concentrations were found to be too high as it caused

urea formation and a decrease in urethane bonds shown in the FTIR spectrum. Therefore, a balance between the loading of TBD, reaction time, and temperature was needed to be able to control unwanted urea formation while also still reacting the CC groups and maintaining the urethane bonds. Nonetheless, these reactions did show the CC peaks decreasing, indicating that the reaction between the PHU prepolymer and A-POSS was occurring.

Table 2: Summary of the main reaction conditions for the synthesis of preliminary HPHUs

Sample	TBD (mol%)	POSS (wt%)	Time (hr)	Temp (°C)
DGC-PHU-4	-	-	24	120
HPHU-A3.1	20	25	5	120
HPHU-A3.3	5	25	5.5	120
HPHU-A3.4	2.5	25	5.5	120
HPHU-A3.7	2.5	25	24	80

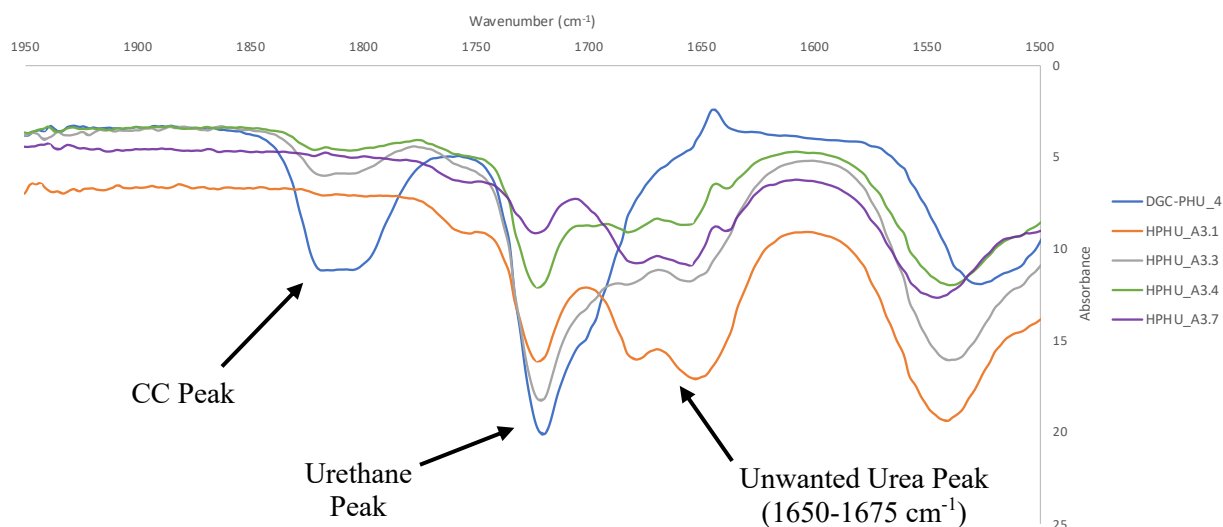
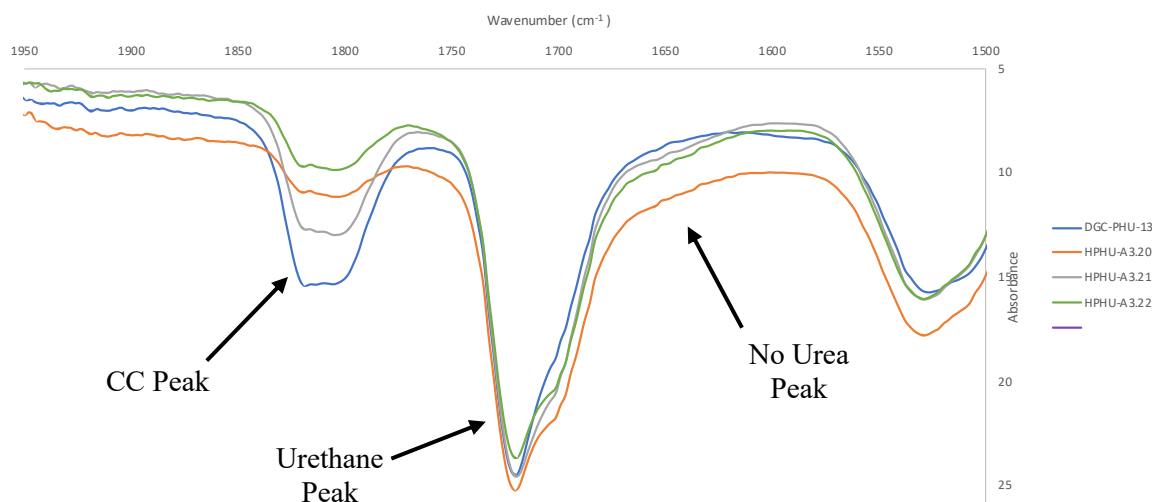
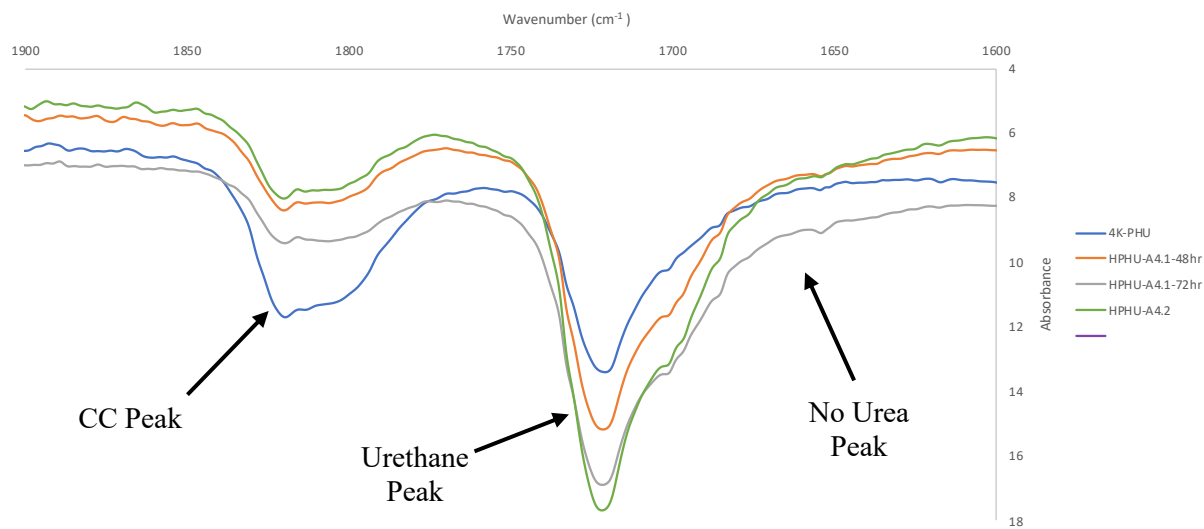


Figure 12: Normalized FTIR results for initial HPHU synthesis reactions with TBD from 1500 cm^{-1} to 1950 cm^{-1}

From here, several different formulations were investigated, and the optimal reaction conditions were found to be adding 0.5 mol% of TBD and stoichiometric amounts of A-POSS (25 wt%) for 24 h at 100 °C. **Table 3** gives a summary of the reaction conditions for the successful HPHUs. Both Jeffamine D-2000 and D-4000 based HPHUs were successfully synthesized and their resulting FTIR spectrums are given in **Figure 13** and **Figure 14**, respectively. In both spectrums, the CC peak is diminishing as compared to the PHUs (both shown in blue) and there are slight increases in the urethane peaks. Furthermore, there is no urea peak being formed, hence indicating the successful addition of A-POSS to form HPHUs.

Table 3: Summary of the main reaction conditions for the synthesis of successful HPHUs

Sample	Jeffamine	TBD (mol%)	POSS (wt%)	Time (hr)	Temp (°C)
DGC-PHU-13	D-2000	-	-	24	120
HPHU-A3.20	D-2000	0.5	25	24	100
HPHU-A3.21	D-2000	0.5	25	24	100
HPHU-A3.22	D-2000	0.5	25	24	100
4K-PHU	D-4000	-	-	28	120
HPHU-A4.1-48h	D-4000	0.5	25	48	100
HPHU-A4.1-72h	D-4000	0.5	25	72	100
HPHU-A4.2	D-4000	0.5	25	72	100

**Figure 13:** FTIR results for successful HPHU synthesis reactions with TBD from 1500 cm^{-1} to 1950 cm^{-1} for Jeffamine D-2000 based HPHUs**Figure 14:** FTIR results for successful HPHU synthesis reactions with TBD from 1600 cm^{-1} to 1900 cm^{-1} for Jeffamine D-4000 based HPHUs

4.2.2 GPC Results

GPC was used to determine the number average molecular weights (M_n) of the POSS modified HPHUs. This revealed if the molecular weight was increasing after the addition of POSS to the PHU prepolymers, giving another indicator if the reaction was successful or not. Though GPC alone is not sufficient to conclude if the reaction was successful, when combined with the FTIR results and other characterizations methods an informed conclusion can be made. **Table 4** summarizes the GPC results relative to PMMA standards and gives the average and absolute M_n values. The absolute M_n values for the HPHUs were calculated based on the absolute M_n of the PHU prepolymers (given in **Table 1**) from the following equation:

$$M_{n,HPHU}^{absolute} = M_{n,PHU}^{absolute} + (2 \times M_{n,APOSS})$$

where the molecular weight of A-POSS is 874.6 g/mol. These molecular weights were then used for subsequent end-capping reactions. Overall, the results show monomodal increases of 2,000 – 5,000 g/mol from the PHU to the HPHUs, which corroborates the FTIR findings that the A-POSS is successfully being incorporated into the polymers.

Table 4: Average and absolute molecular weights of synthesized HPHUs

Sample	Jeffamine	Time (hr)	Average M_n (g/mol)	Dispersity (Đ)	Absolute M_n (g/mol)
DGC-PHU-13	D-2000	24	5,900	2.15	6,900
HPHU-A3.20	D-2000	24	7,500	1.74	8,600
HPHU-A3.21	D-2000	24	7,800	1.82	8,600
HPHU-A3.22	D-2000	24	9,900	1.77	8,600
4K-PHU	D-4000	28	5,900	1.99	8,700
HPHU-A4.1-48h	D-4000	48	9,300	1.58	10,400
HPHU-A4.1-72h	D-4000	72	11,100	1.54	10,400
HPHU-A4.2	D-4000	72	10,000	1.59	10,400

To further illustrate these findings, **Figure 15** shows the GPC plot for a successful HPHU reaction (based on the FTIR results) compared to its corresponding PHU prepolymer (shown in blue). This graph shows the HPHU immediately after the reaction was completed (referred to as HPHU-A3.16 and shown in orange) and then the same HPHU after it was left to settle out for 6 weeks (referred to as HPHU-A3.16-TOP and shown in grey). HPHU-A3.16 shows a large peak to the right, which corresponds to the unreacted A-POSS within the polymer mixture. After letting the sample settle and taking a GPC sample from the upper phase, this peak disappears and a shift to the left is observed, which indicates an increase in the molecular weight. This confirms that the

increase in molecular weight that is observed is not coming from unreacted A-POSS in the polymer mixture, but rather from the A-POSS being covalently bonded to the PHU.

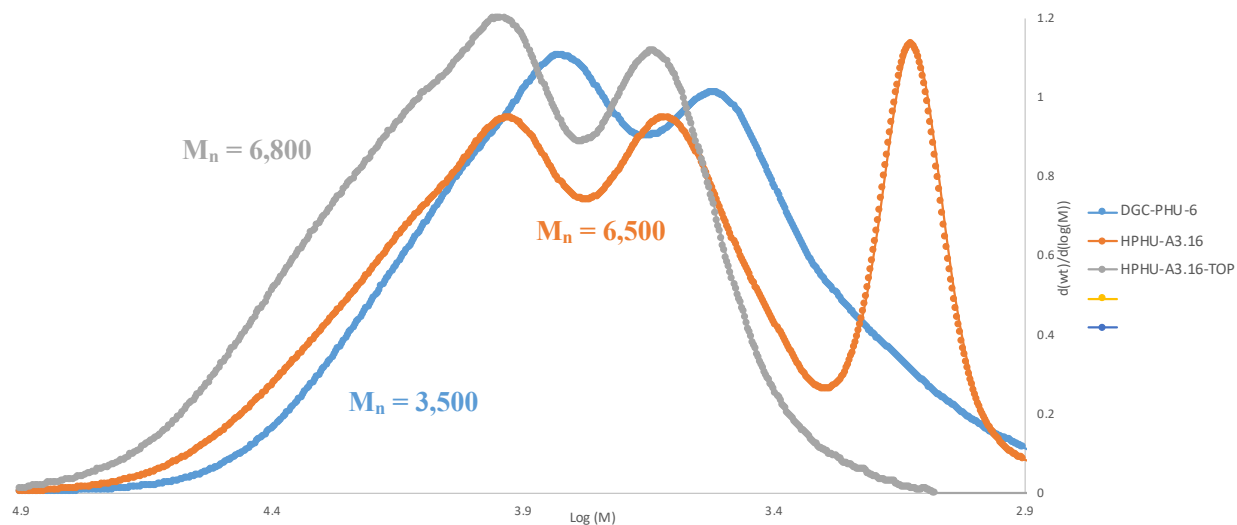


Figure 15: GPC results for HPHU-A3.16 immediately after reaction (orange) and left to settle for 8 weeks (grey) as compared to DGC-PHU-6

Figure 16 also gives the GPC plot for the HPHU-A4.1 reactions at different times throughout the reaction. This figure shows the plots shifting to the left as the reaction time increases, indication the increase in molecular weight. Additionally, there are no peaks appearing for A-POSS, signifying that there is little to no unreacted A-POSS in the HPHUs.

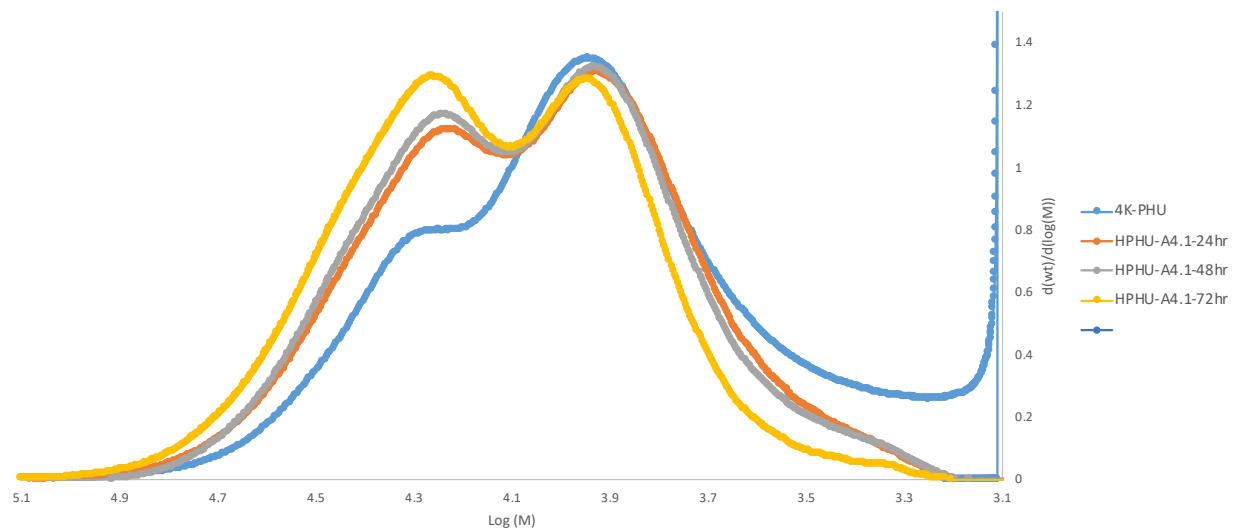


Figure 16: GPC results for HPHU-A4.1 reactions at 24, 48, and 72 h as compared to 4K-PHU

4.2.3 NMR Results

Finally, ^1H and ^{29}Si NMR tests were performed to obtain information about the molecular structure beyond just the functional groups. This was used to further confirm the successful synthesis of the A-POSS modified HPHUs. Predicted ^1H NMR spectrums were utilized to aid in the deconvolution of peaks as well as to provide a basis for the real ^1H NMR spectrums. **Figure 17** provides the predicted ^1H NMR for A-POSS along with the labelled structure. The key peak for this spectrum is group A, shown in red, which represents the protons next to the amine group. When the amine group is reacted, the neighbouring protons in group A will experience a different chemical shift and therefore this peak at 2.65 ppm is expected to disappear.

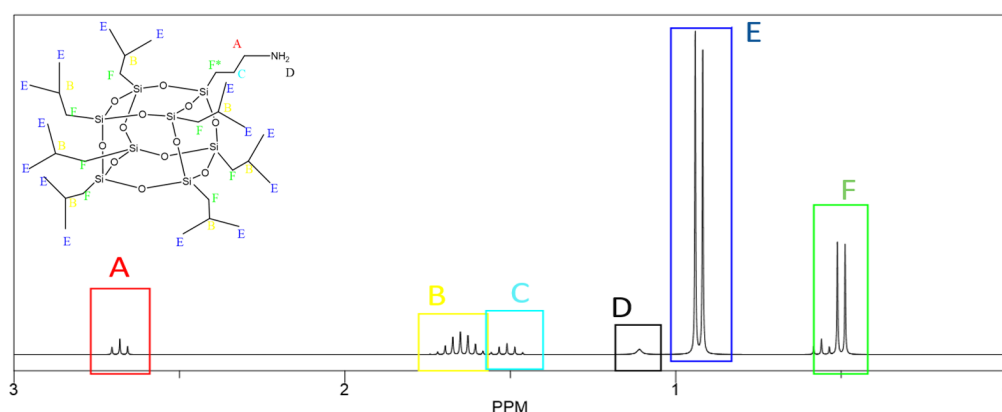


Figure 17: Predicted ^1H NMR Spectrum for A-POSS

Figure 18 gives the experimental ^1H NMR results for the A-POSS (top), the HPHU (middle), and the PHU prepolymer (bottom). When comparing these spectra, the HPHU has all the peaks from the PHU, but also shows peaks that correspond to the A-POSS at 0.6, 0.95, and 1.8 ppm. Furthermore, there is no peak appearing at 2.65 ppm for the HPHU spectrum, which corresponds to the red group A of the A-POSS noted in **Figure 17**. Since this peak is not appearing, but all other major peaks of the A-POSS are, this further confirms the successful addition of A-POSS into the HPHU.

To take it one step further, ^{29}Si NMR was also conducted to further confirm the addition of A-POSS. This test was performed on the HPHU sample that was left to settle for over 6 weeks and only the top was taken for analysis. GPC analysis was also performed on the same sample to ensure that no A-POSS peak was appearing. **Figure 19** gives the HMBC between ^1H and ^{29}Si and shows a 2D plot with the ^1H signal in the horizontal and the ^{29}Si signal in the vertical. The red contours shown in this plot indicate Si elements that are detected. These appear at 0.6, 0.95, and 1.8 ppm

on the horizontal ^1H dimension and around 65-70 ppm in the vertical ^{29}Si dimension. The values in the ^1H dimension are consistent with the results in **Figure 17** and **Figure 18**. Additionally, the chemical shifts shown in the ^{29}Si dimension are consistent with values reported for Si-O-Si POSS cages in literature [59]. Since this sample is free from unreacted A-POSS, and the PHUs alone do not contain any Si molecules, it can be concluded that the Si detected in this plot is a result of the A-POSS that has been covalently bonded to the PHUs.

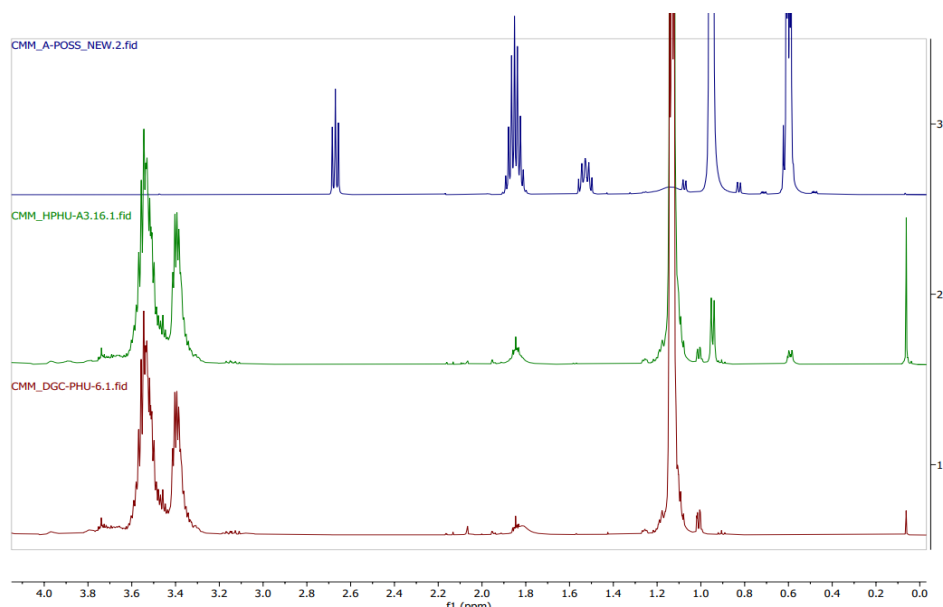


Figure 18: ^1H NMR results for A-POSS (top), HPHU (middle), and PHU (bottom)

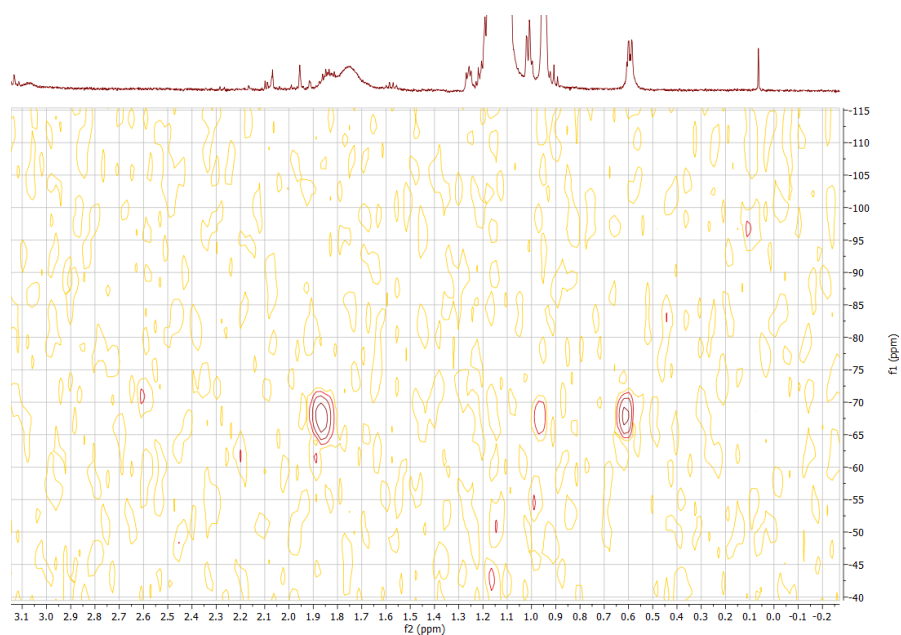


Figure 19: HMBC between ^1H and ^{29}Si NMR spectrum for uncured HPHU

4.2.4 TGA & DSC Results

TGA and DSC were performed on the HPHUs to determine the thermal properties of the liquid polymers. TGA provides the degradation of the material as a function of temperature and elucidates at what temperatures the polymers degrade. DSC, on the other hand, provides information such as the T_g and melting temperatures T_m . **Table 5** summarizes the degradation temperatures (T_d) at 1, 10, 50, and 85 wt% of weight loss for the Jeffamine D-2000 PHU/HPHUs and **Figure 20** shows the resulting TGA plot. The PHU prepolymer (referenced as DGC-PHU-6 and shown in blue) has the lowest onset degradation temperature ($T_{d,onset}$) and the steepest slope, indicating that it rapidly degrades after $T_{d,onset}$. The two HPHUs (HPHU-A3.17-TOP and HPHU-A3.17-MIX shown in grey and orange, respectively) show slightly higher T_d values and give more moderate slopes with the MIX HPHU displaying the highest T_d values. This shows that the addition of A-POSS increases the thermal degradation with a substantial increase with additional unreacted A-POSS within the HPHUs.

Table 5: TGA Results for uncured Jeffamine D-2000 PHU/HPHUs

Sample	T_d 1% (°C)	T_d 10% (°C)	T_d 50% (°C)	T_d 85% (°C)
DGC-PHU-6	123.5	225.8	263.8	287.4
HPHU-A3.17-MIX	186.2	268.5	341.4	376.8
HPHU-A3.17-TOP	135.2	237.4	288.3	337.4

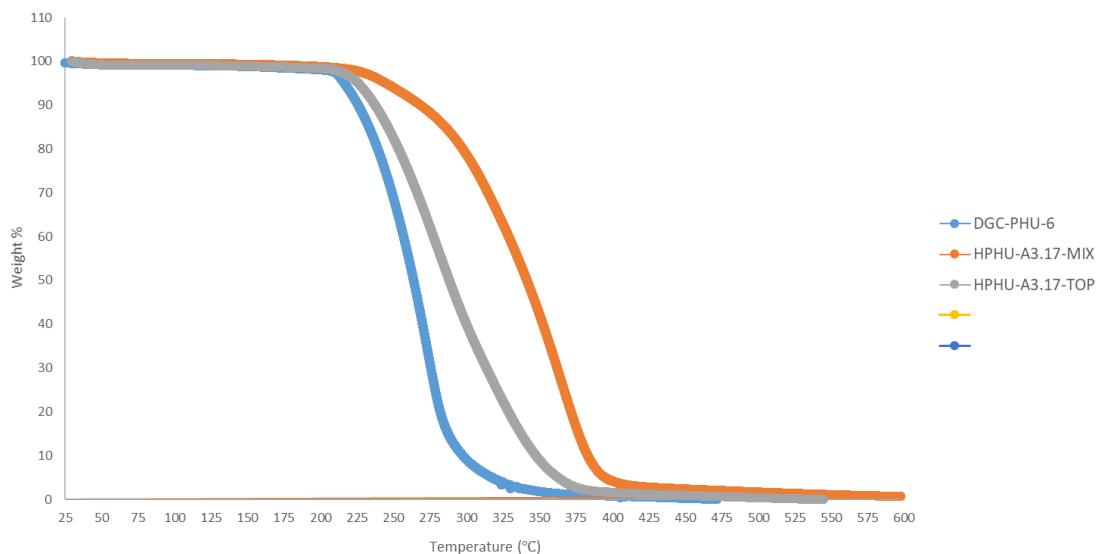


Figure 20: TGA results for Jeffamine D-2000 based PHU and HPHUs

DSC was also performed to determine the T_g of the HPHUs and their PHU counterparts. These results are provided in **Table 6**. Heat-cool-heat experiments were performed to ensure that the resulting T_g is unaffected by the thermal history of the polymer. The T_g values obtained are consistent and only slight deviations are observed between the PHU and HPHUs. However, there is about a 5 °C difference between the Jeffamine D-2000 and Jeffamine D-4000 polymers. This can be explained by the difference in the chain lengths of these monomers, which affects the flexibility of the polymers resulting in different T_g values.

Table 6: Summary of T_g values for uncured PHU/HPHUs

Diamine	Sample	T_g (°C)
Jeffamine D-2000	DGC-PHU-6	-61.7
	HPHU-A3.16-TOP	-62.6
	HPHU-A3.17-MIX	-61.8
Jeffamine D-4000	4K-PHU	-66.3
	HPHU-A4.2-TOP	-67.1

4.2.5 Steady Shear Viscosity Results

Finally, steady shear viscosity tests were performed on the PHUs and HPHUs to evaluate their physical properties. **Figure 21** shows the results for the viscosity tests for the tested samples. The highest viscosities recorded were 44.7 and 35.9 Pa·s, corresponding to HPHU-A3.21-MIX and HPHU-A3.21-TOP, respectively. These samples were the Jeffamine D-2000 based HPHUs. The next highest recorded viscosity was 16.6 Pa·s, which corresponds to the Jeffamine D-4000 HPHU-A4.2-TOP. Finally, the two PHU prepolymers, DGC-PHU-13 and 4K-PHU were found to have viscosities of 9.2 and 5.9 Pa·s. The Jeffamine D-2000 based HPHUs has the highest viscosities, which is understandable as this Jeffamine is a shorter chain diamine with less flexibility and therefore a higher viscosity. Moreover, the viscosities for all the HPHUs were higher than their PHU counterparts, demonstrating the physical change incorporating the A-POSS produces. These values are also comparable to ADFASTs current PU sealant formulation, which has a viscosity of 20 Pa·s. This is important as the maximum viscosity that ADFAST can mix in their reactor is 2,000 Pa·s, however the desirable range is from 10-500 Pa·s. The HPHU formulations fall within the desirable viscosity which make them ideal for future scale up.

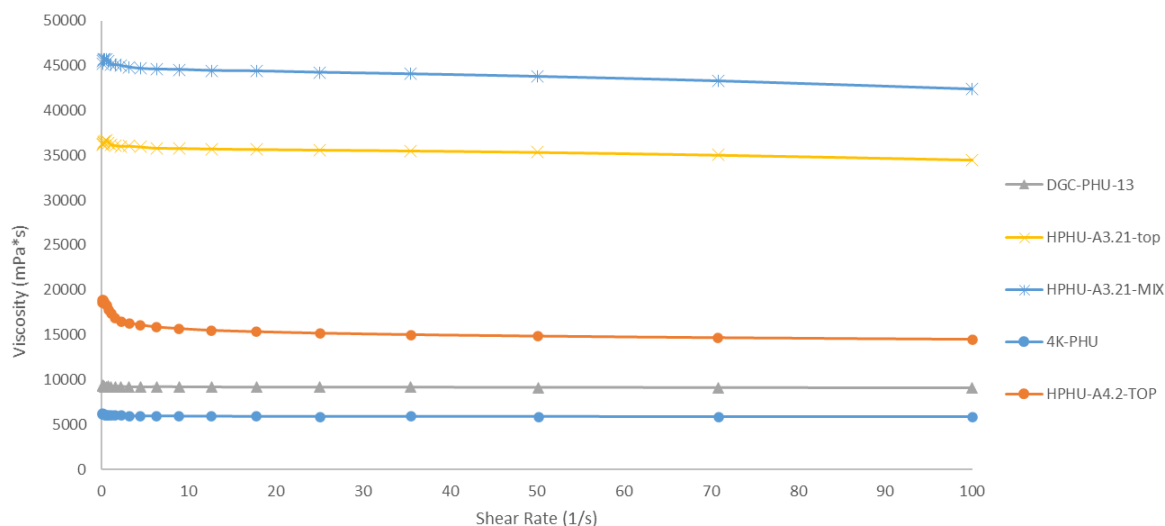


Figure 21: Steady Shear Viscosity comparison of Jeffamine D-2000 PHU/HPHUs to Jeffamine D-4000 PHU/HPHUs

4.3 Curing Synthesis and Characterization

4.3.1 Polymer Blends

Now that the Amino POSS has been shown to be successfully incorporated into the polymer, the next focus was on blending. In this method, the goal was to be able to blend the POSS-based PHUs with silane end capped PHUs to obtain a final cured film with POSS incorporated throughout. Since the HPHU and PHU have the same backbone, in principle, they should be miscible with each other, and can thus be blended to obtain a polymer with properties of each component. This was investigated as the HPHU synthesis end caps the PHU with POSS, leaving no more terminal sites for further moisture curing modifications. Consequently, blending with a PHU that has been modified with silane moisture curable groups would allow for a final cured polymer. DAMO, which is an amino functional silane, was used as the moisture curable end-capper for the PHU and is shown above in **Scheme 6**.

To do this, DGC-PHU was first allowed to react with DAMO to determine the base conditions for this reaction, such that curing in ambient conditions could occur. This reaction uses the CC end groups of the PHU to react with the primary amine in DAMO to obtain an end-capped polymer. The optimal conditions were found to be 90 °C for 20 min, which was then used for subsequent blending reactions. Next, HPHU-A3.17 was added at 10, 20, and 40 wt% with stoichiometric

amounts of DGC-PHU and DAMO and allowed to react at the same conditions. **Figure 22** gives the FTIR spectrum for the DGC-PHU compared to the DGC-PHU with DAMO and the A3.17-20% Blend. This shows the CC carbonate peak around 1800 cm^{-1} has completely disappeared for both reactions, indicating that the DAMO was successfully reacted with the PHU. Furthermore, there is an increase in the urethane peak around 1720 cm^{-1} which correlates to the urethane bond being formed between the CCs of the PHU and the amine of the DAMO.

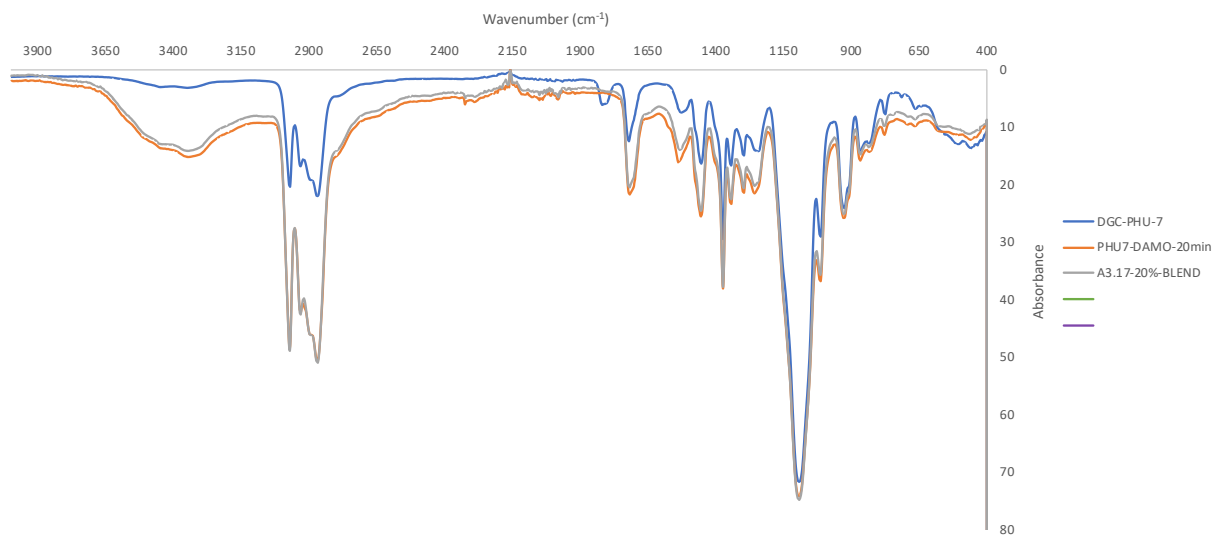


Figure 22: FTIR Results for PHU-DAMO-20min and HPHU-A3.17-20%-Blend compared to DGC-PHU7

4.3.1.1 Gel Content Tests

Gel content is an important test that is used to quantify the degree of crosslinking in cured polymers. Gel content tests, as described in section 3.3.6, were conducted and the results are given in **Table 7**. The PHU-DAMO reactions gave gel contents from 41-43%, while the HPHU blends gave gel contents from 24-38%. The lower gel content for the blends can be attributed to the fact that no moisture-sensitive silane groups are borne by HPHU-A3.17, therefore significantly reducing the cross-linking density. Moreover, the swelling indices for the blends were much higher than that of the PHU-DAMO samples, which is a direct correlation of the low cross-link density. When the cross-link density is low there is more space/availability for the THF to penetrate the sample and cause it to swell. Overall, this method of polymer blending gave unfavourable results as the gel contents were too low to get solid samples suitable for mechanical testing. Thus, a different method to cure the polymers was investigated and will be discussed in the following sections.

Table 7: Gel Content Tests for Polymer Blends

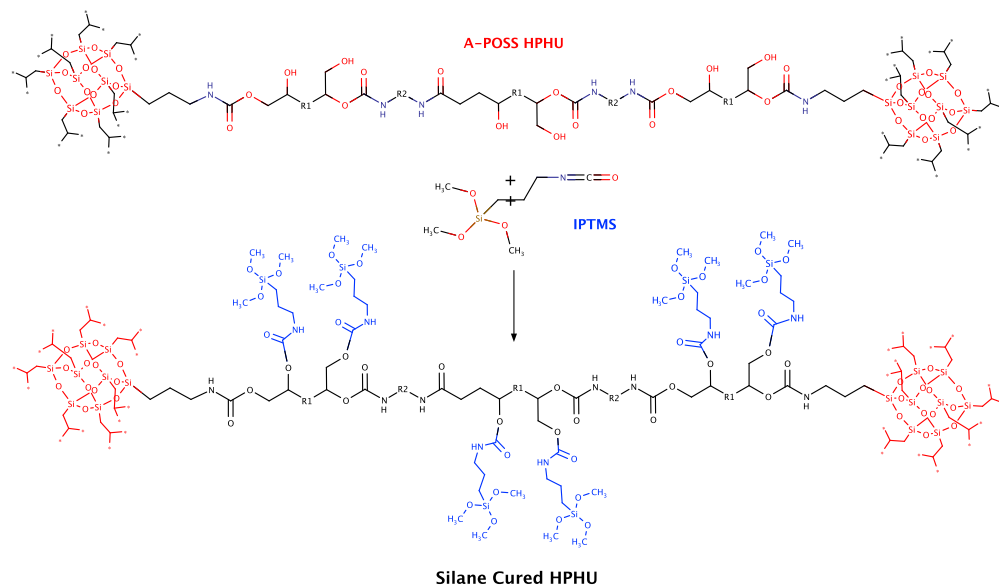
Sample	Gel Content	Swelling Index
PHU-DAMO-20min	43%	327%
PHU-DAMO-30min	41%	304%
A3.17-10%-Blend	38%	420%
A3.17-20%-Blend	28%	364%
A3.17-40%-Blend	26%	480%

4.3.2 Silane End-Capping

In the previous section, blending the A-POSS hybrid polymer (from 10-40 wt%) with a PHU prepolymer capped with DAMO was explored and found to be unsuccessful. Therefore, IPTMS was then investigated to cap the pendant hydroxyl groups within the backbone of the polymer. This method results in a PHU backbone, end-capped with A-POSS and IPTMS attached throughout the backbone as shown in **Scheme 9**. This reaction takes advantage of the reactive OH/NCO pair, which converts the pendant hydroxyl group to a carbamate linkage and thus increases the hydrophobicity. The maximum molar ratio of IPTMS used was 10:1 as there is approximately 10 -OH groups in the HPHUs (calculation provided in Appendix A). This molar ratio along with 5:1 was investigated for the HPHUs/PHUs with Jeffamine D2000 in the backbone. Next, a ratio of 10:1 was explored again, but this time with HPHUs/PHUs with Jeffamine D4000 in the backbone. **Table 8** gives an overview of the experiments that have been conducted below (Note that this table provides the full sample names along with corresponding sample numbers and the sample set – in subsequent tables the sample names may be shortened for ease of reading, but the corresponding No. and Set will always be provided for reference). Characterization methods and testing for these samples will be presented and discussed in the following sections.

Table 8: Summary of Silane End-Capping Reactions

Set	No.	Sample	Jeffamine	IPTMS:PHU	POSS wt%	Time (hr)	Temp
	1	PHU-IPTMS-7	D-2000	10:1	0	24	120
1	2	A3.20-TOP-IPTMS	D-2000	10:1	25	24	100
	3	A3.20-MIX-IPTMS	D-2000	10:1	25	24	100
	4	PHU-IPTMS-8	D-2000	5:1	0	24	120
2	5	A3.21-TOP-IPTMS	D-2000	5:1	25	24	100
	6	A3.22-MIX-IPTMS	D-2000	5:1	25	24	100
	7	4K-PHU-IPTMS	D-4000	10:1	0	28	120
3	8	A4.2-TOP-IPTMS	D-4000	10:1	25	72	100
	9	A4.1-MIX-IPTMS	D-4000	10:1	25	72	100



Scheme 9: Synthesis of cured A-POSS HPHU films using IPTMS functional silane

4.3.2.1 FTIR Results

FTIR was performed to ensure that there was no unreacted isocyanate within the cured samples. **Figure 23** shows the spectra for previous samples at 5:1, 8:1, and 10:1 ratio of IPTMS:PHU. The peak for isocyanate appears around 2270 cm^{-1} . As shown, none of the spectra's have this peak, even at the maximum concentration of IPTMS at 10:1. Therefore, it can be concluded that no samples have unreacted IPTMS and thus, no isocyanates within the samples.

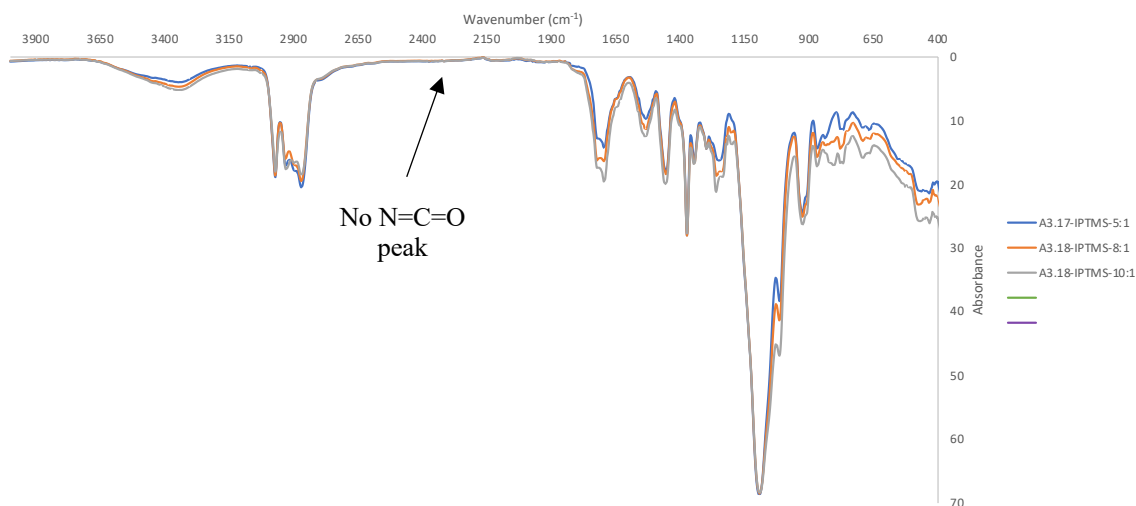


Figure 23: FTIR spectrum of cured HPHUs with 5:1, 8:1 and 10:1 ratio of IPTMS:HPHU showing no isocyanate peaks

FTIR was also used to verify that the IPTMS was in fact reacting with the pendant -OH groups of the polymer backbone rather than the CC end groups. **Figure 24** shows the FTIR spectrum for the PHU prepolymer compared to the silane modified PHU:IPTMS at a 1:8 ratio. This spectrum shows that the peak for the CC end groups of the PHU prepolymer at 1800 cm^{-1} is unchanged, while the urethane peak at 1720 cm^{-1} is increased. Moreover, there is also an increase in the NH bend at 3330 cm^{-1} and 1530 cm^{-1} as well as a decrease in the OH peak at 1012 cm^{-1} . This confirms that IPTMS is not reacting with the CC groups but is reacting with the OH groups to form additional urethane bonds. Overall, these results show that IPTMS is successfully being introduced into the polymer matrix to give moisture curable HPHU films.

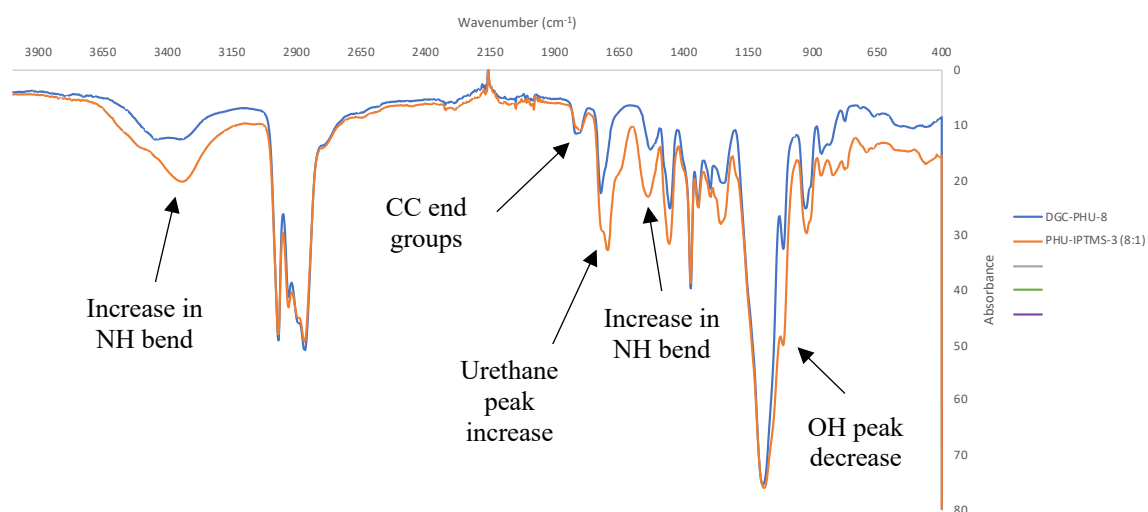


Figure 24: FTIR spectrum of PHU prepolymer (blue) compared to cured PHU-IPTMS (orange) at 8:1 ratio IPTMS:PHU

4.3.2.2 Gel Content Results

Once the samples were reacted with IPTMS and left to cure, gel content tests in THF were performed and the results are given in **Table 9**. The first set of reactions had gel contents from 87-99% with the highest being PHU-IPTMS-7, which has no A-POSS. However, PHU-IPTMS-7 also had the highest swelling index, while A3.20-IPTMS-MIX had the lowest. This can be attributed to the hydrophobic nature of A-POSS as A3.20-IPTMS-MIX has the highest amount of A-POSS. The second set of tests also showed good gel contents at 90% with a slight increase in the swelling index due to the lower IPTMS concentration. Finally, the third set with Jeffamine D-4000 and a 10:1 ratio of IPTMS gave similar gel contents, but higher swelling indices. The increase in swelling is due to the longer chain diamine that is used as there is more surface for the THF to

penetrate the polymer and cause it to swell. **Figure 25** illustrates the relationship of the swelling index for these samples. This highlights how changing the diamine as well as the IPTMS and POSS concentrations affects swelling of the polymer. Overall, the cured films exhibited excellent gel contents with values from 87-99%. This exceeds what has previously been reported in literature as linear NIPUs were found to only have gel contents around 67% [58].

Table 9: Gel Content Results for Silane End-Capping

Set	No.	Ratio/Diamine	Sample	Gel Content	Swelling Index
1	1	Jeff 2000 - 10:1	PHU	99%	123%
	2		TOP HPHU	92%	112%
	3		MIX HPHU	87%	104%
2	4	Jeff 2000 - 5:1	PHU	93%	149%
	5		TOP HPHU	90%	160%
	6		MIX HPHU	90%	155%
3	7	Jeff 4000 - 10:1	PHU	98%	180%
	8		TOP HPHU	91%	188%
	9		MIX HPHU	87%	138%

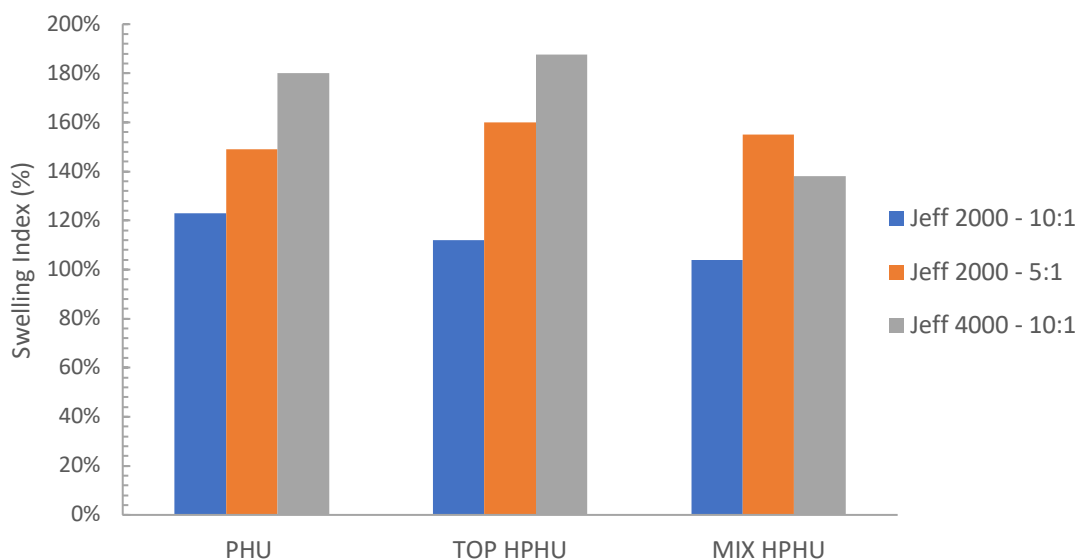


Figure 25: Swelling index for cured PHU and HPHUs

4.3.2.3 Water & Toluene Swelling

Gel content tests in water and toluene were also performed to investigate the effect POSS had on the swelling of the polymers. Due to the hydrophobic nature of POSS, swelling in water is expected to be reduced for the HPHUs compared to the PHUs. Additionally, POSS is known to swell in toluene [60] and thus, the swelling index in toluene is expected to be greater for the HPHUs compared to the PHUs. **Table 10** summarizes the gel contents and swelling index found

for sample sets 1 and 3 in water and toluene. These results agree with the hypothesis as the swelling index in water for the HPHU is much less than that for the PHU. Conversely, the swelling index in toluene is greater for the HPHUs as compared to the PHUs. This further confirms the successful incorporation of A-POSS into the polymer network as sample No.2 TOP HPHU (which has no unreacted A-POSS) exhibits the swelling behaviours of POSS. Moreover, these results also show very low swelling indices in water for both HPHUs, indicating that they repel water, which is a desired property for PU sealants.

Table 10: Gel Content and Swelling in Water and Toluene Results

Set	No.	Ratio/Diamine	Sample	Toluene		Water	
				Gel Content	Swelling Index	Gel Content	Swelling Index
1	1	Jeff 2000 - 10:1	PHU	>99%	121%	>99%	58%
	2		TOP HPHU	99%	185%	>99%	10%
3	7	Jeff 4000 - 10:1	PHU	>99%	123%	>99%	32%
	9		MIX HPHU	91%	174%	>99%	9%

4.3.2.4 Curing Kinetics

Curing kinetic studies were performed on the PHU and HPHUs capped with IPTMS to determine the gel time, or when the film began to form. As described in section 3.2.4, a proprietary tin-based catalyst from ADFAST was added to the reactor after the IPTMS reaction to accelerate the curing reaction in ambient conditions. All curing reactions utilized this catalyst and thus all curing kinetic studies were performed with this catalyst as well. Without the catalyst, the curing reaction took well over 6 weeks to fully cure, where curing overnight was observed with the catalyst. **Figure 26** and **Figure 27** show the results for these curing kinetic studies for the Jeffamine D-4000 based PHU/HPHUs and Jeffamine D-2000 based HPHUs, respectively. The gel time is observed when the storage modulus (G') and loss modulus (G'') intersect and is indicated with a $\times$ in the figures below. **Figure 26** shows the comparison of the 4K-PHU-IPTMS (sample No. 7) vs. A4.2-TOP-IPTMS (sample No. 8) and gel times of 1 h and 52 min are observed, respectively. Next, **Figure 27** shows the comparison of A3.21-TOP-IPTMS (sample No. 5) vs. A3.22-MIX-IPTMS (sample No. 6), which are the samples with a 5:1 ratio of IPTMS. The gel times for these reactions were found to be 30 min and 57 min for the TOP-HPHU and MIX-HPHU, respectively. These short gel times can be explained by the elevated relative humidity of 60% in the ambient environment, which accelerated the curing due to the high amounts of water in the air. The other curing studies were completed at lower humidity's around 20-35%. Overall, all reactions had gel

times under 1 h and fully cured films were observed in 24 h. This is much lower than previously reported curing times for HNIPU coatings of 7 days [7] and is within the curing time of 13-36 h for typical PU sealants [61].

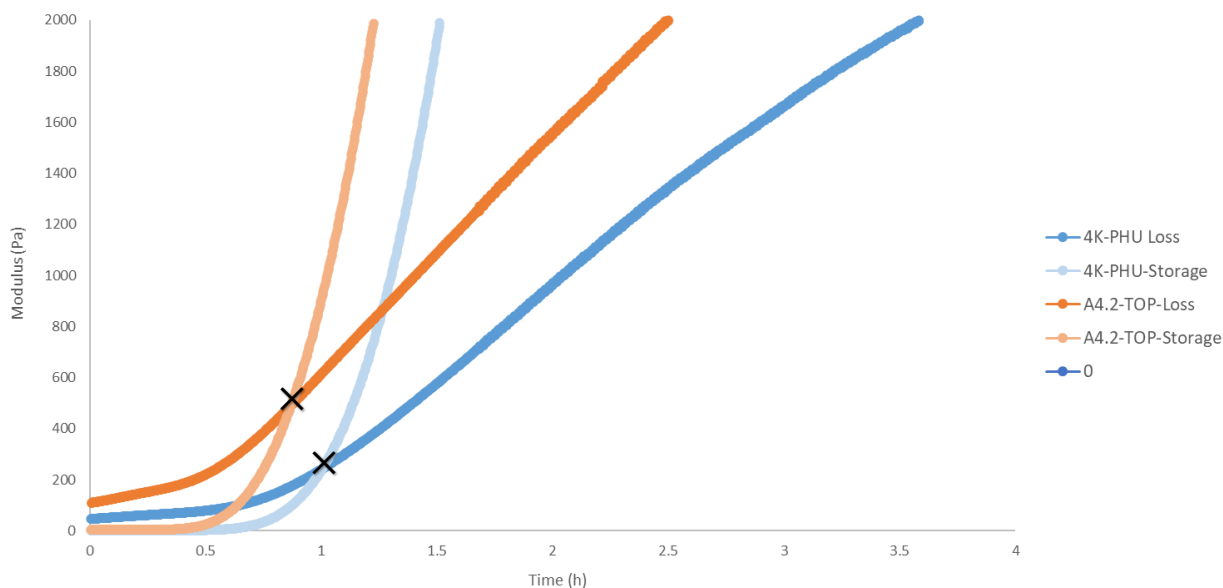


Figure 26: Curing kinetics of Jeffamine D-4000 PHU/HPHUs. 4K-PHU (blue) and HPHU-A4.2-TOP (orange) with 10:1 ratio of IPTMS

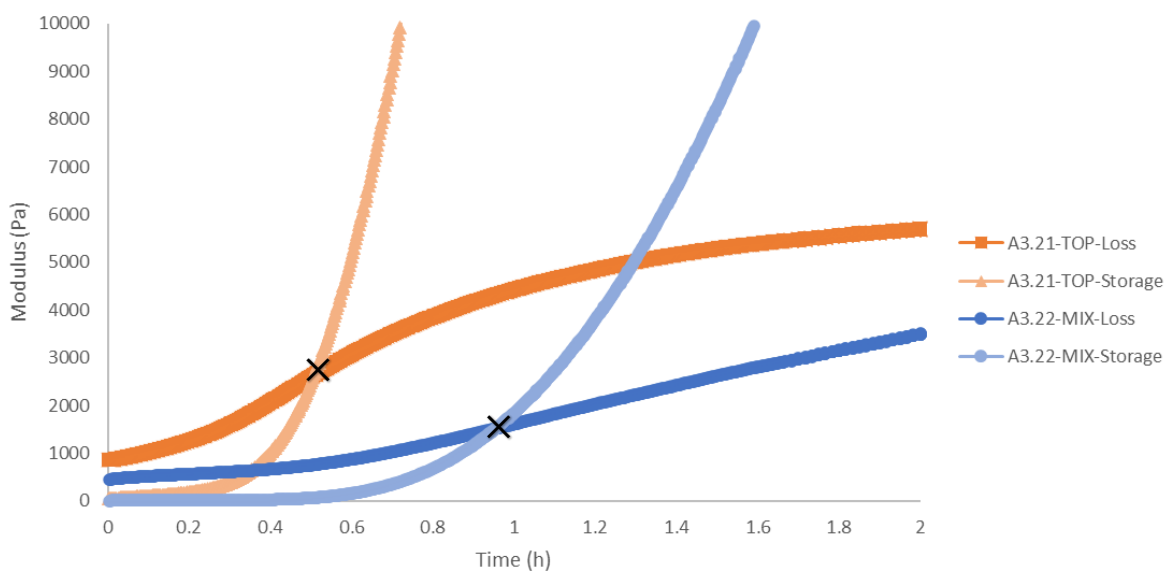


Figure 27: Curing Kinetics of Jeffamine D-2000 HPHUs. A3.21-TOP (orange) vs A3.22-MIX (blue) with 5:1 ratio of IPTMS

4.3.2.5 TGA & DSC Results

TGA and DSC was performed on the cured polymers to determine the thermal properties of the films. **Table 11** summarizes the degradation temperatures (T_d) at 1, 10, 50, and 85% for sample sets 1 and 3 with the highest and lowest temperatures highlighted in green and red. Sample No.9, the Jeffamine D-4000 MIX HPHU, displayed the best thermal stability as it had the highest degradation temperatures overall. However, the differences between the T_d for the cured polymers are minimal as shown in **Figure 28**. The incorporation of IPTMS into the PHU/HPHUs increased the thermal stability overall as higher T_d values were recorded for the cured polymers as compared to the uncured (given in **Table 5**). Nonetheless, the mixed HPHUs, both cured and uncured, gave the best performance in terms of thermal degradation, thus it can be concluded that the addition of A-POSS enhances the thermal stability of the PHUs.

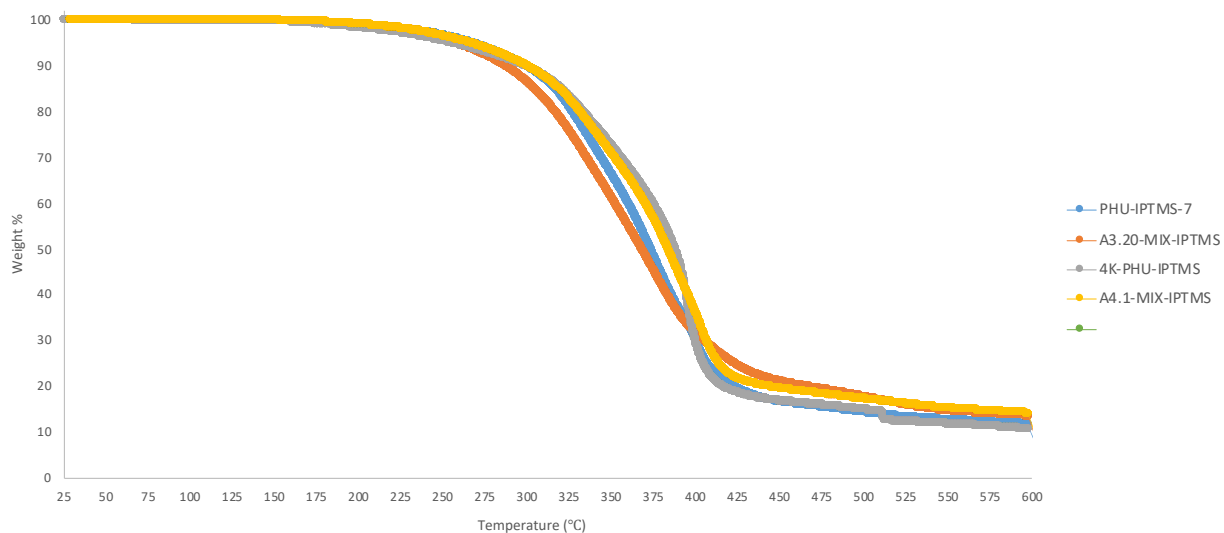


Figure 28: TGA results for cured PHUs and MIX HPHUs

Table 11: TGA Results for Cured Polymers

Set	No.	Sample	Ratio/Diamine	T_d 1% (°C)	T_d 10% (°C)	T_d 50% (°C)	T_d 85% (°C)
1	1	PHU	10:1 Jeff 2000	195.3	298.9	373.5	485.2
	2	TOP HPHU		197.7	296.3	366.7	526.5
	3	MIX HPHU		189.8	286.6	368.2	541.4
3	7	PHU	10:1 Jeff 4000	176.3	298.1	388.1	498.9
	8	TOP HPHU		184.5	290.6	378.2	466.7
	9	MIX HPHU		197.9	299.3	383.9	560.7

DSC was the next test that was completed to determine the T_g and T_m values for the polymers. **Table 12** gives a summary of the T_g values for the Jeffamine D-4000 cross-linked polymers below. The T_g values were consistent as only a 2 °C difference was observed between the PHU and HPHUs. This small increase could be due to the addition of POSS cages at the nanometer level, which restrict the motion of macromolecular chains as shown in other POSS-modified polymers [53, 55]. Furthermore, these T_g values are very similar to their uncured counterparts given above in **Table 6**. These low T_g values can be attributed to the long chain diamines, as they provide flexibility and make up most of the polymer, thus giving a lower T_g .

Table 12: Summary of T_g values for cured Jeffamine D-4000 based HPHUs

Set	No.	Sample	Ratio/Diamine	T_g (°C)
3	7	PHU	10:1 Jeff 4000	-67.1
	8	TOP HPHU		-65.6
	9	MIX HPHU		-65.6

To illustrate further, **Figure 29** displays the DSC plot obtained for sample No.9 MIX HPHU and shows the T_g and T_m values. The T_m values appear as peaks where the T_g value appears as a step. The T_m in this plot corresponds to the melting of A-POSS as the PHU plots did not have these peaks. Overall, there were insignificant differences in both the cured and uncured polymers in terms of their T_g values, which is attributed to the long-chain Jeffamine monomers that make up most of the polymers.

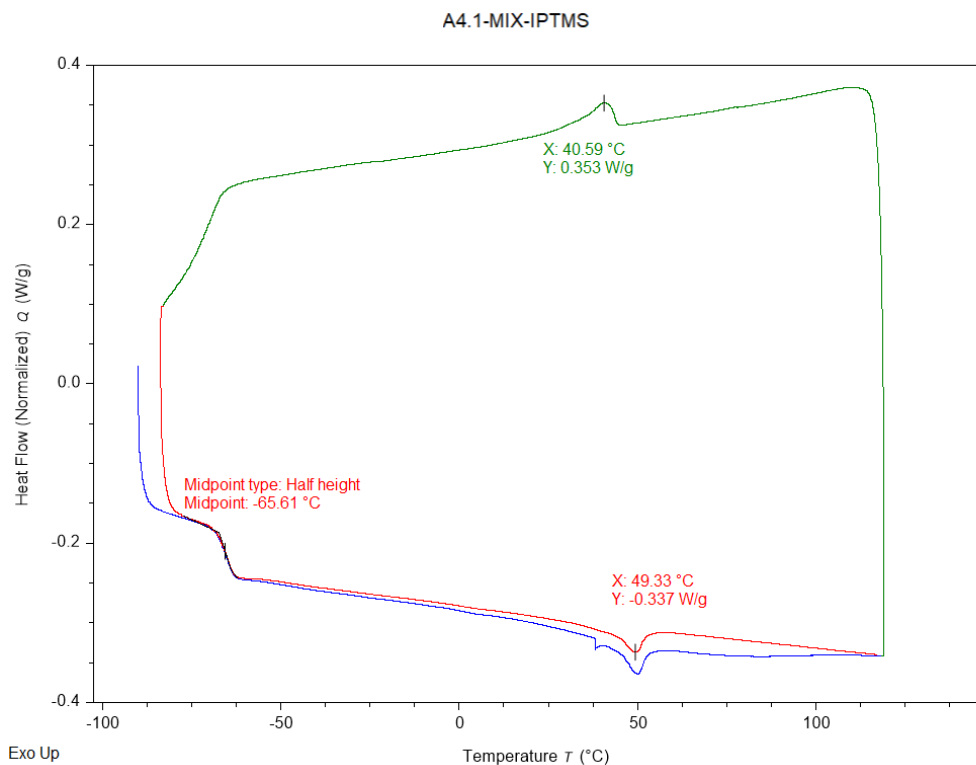


Figure 29: DSC plot of A4.1-MIX-IPTMS showing the T_g and melting points

4.3.2.6 Tensile Testing

Tensile testing was performed to elucidate the mechanical properties of the cured HPHU films. This was useful in determining if adding POSS to the PHUs added strength to the polymer network, which was one of the main goals of this work. The Young's modulus (E), elongation at break (EB%), and tensile strength at break (σ_{max}) were investigated. **Figure 30** shows the stress-strain plot for sample No. 9: MIX HPHU and illustrates how the three variables are calculated. The Young's modulus is found by taking the slope from the linear trendline of the data and is a measure of the elasticity of the material. Specifically, the Young's modulus expresses how easily the polymer can deform or stretch – the higher the Young's modulus, the less it will stretch and deform. EB% is found along the x-axis when the sample ruptures. This variable gives how much the sample can be elongated before rupture as a percentage of the original length. Finally, the tensile strength is found along the y-axis when the sample ruptures and this gives the amount of force that can be applied before the material fails.

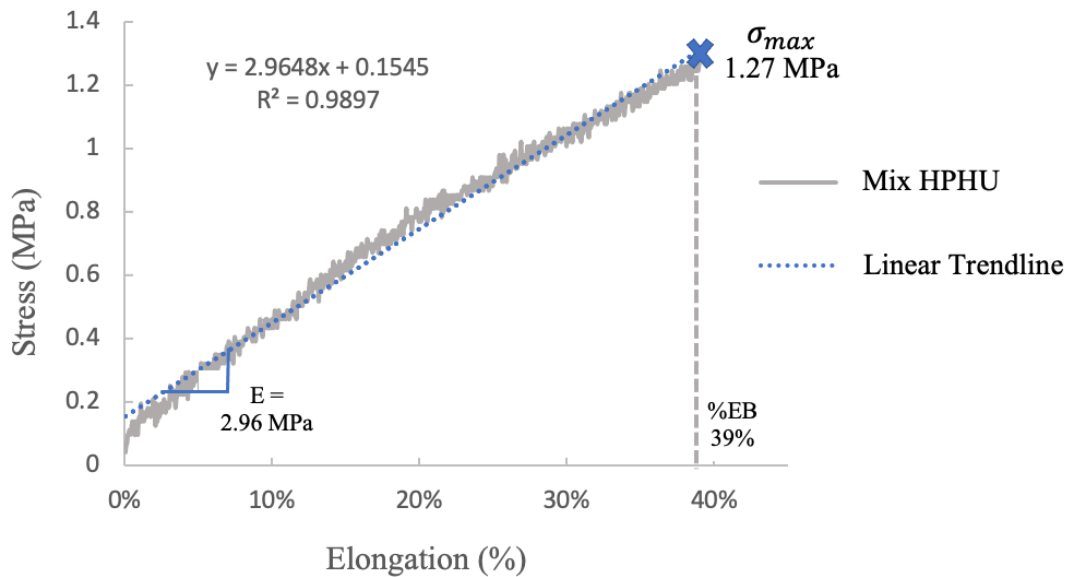


Figure 30: Stress-strain curve for sample No. 9: Mix HPHU

In this work, a balance between elasticity and tensile strength was desired as the goal is to use these HPHUs for sealant applications. **Figure 31** shows a graphical representation of the physical properties for different types of products that ADFAST offers. From this, a polymer with high elasticity and low tensile strength is required, however it may be possible to use the HPHUs for different applications that could be more suitable.

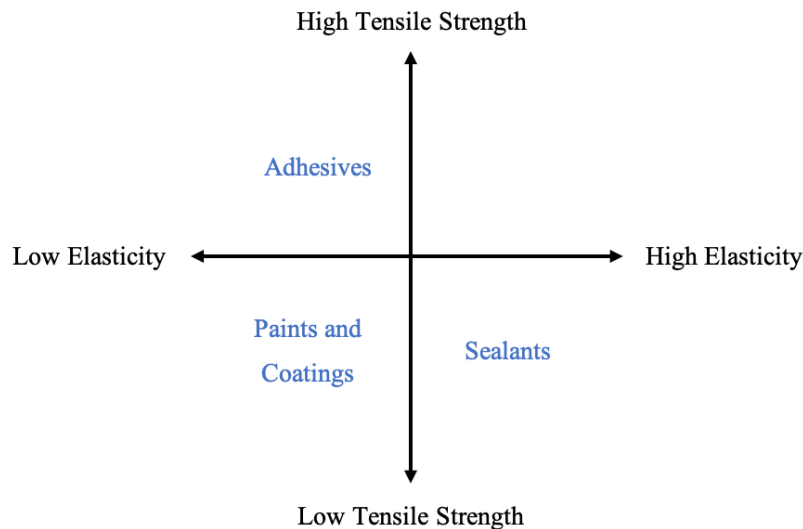


Figure 31: Graphical representation of ADFAST's product markers

To begin, 5-6 dog bone shaped cut-outs were taken for each sample to be analyzed, and the results were averaged to give a single mean value. The results are summarized in **Table 13** and graphical comparisons for the elongation at break, tensile strength, and Young's modulus are given in **Figure 32**, **Figure 33**, and **Figure 34**, respectively. The figures give bar graphs with error bars that correspond to the maximum and minimum values that were recorded for each variable. Additionally, the tensile properties for ADFASTs current isophorone diisocyanate (IPDI) based PU are also given. This PU is the base for many of their commercial sealant products and thus, provides a good benchmark for comparison.

The first set of samples displays high Young's modulus, good tensile strength, but lower elongations at break. For example, sample No.3: MIX HPHU, has the highest Young's modulus of 5.9 MPa but the lowest elongation at break at 16.5%. This is likely due to the unreacted A-POSS in the HPHU during the curing reaction, which imparted brittleness to the material. Sample No.2: TOP HPHU gives a good balance of properties with an increase in all three variables from the PHU in addition to an increase in the tensile strength of almost double compared to ADFASTs PU. However, the elongation at break is still on the lower end.

The next set of samples with a 5:1 ratio of IPTMS and using Jeffamine D2000 gave lower Young's modulus and tensile strength, but similar elongations at break compared to the first set. The increase in strength from the PHU to HPHU was still observed, however the increase between the MIX HPHU and TOP HPHU is much smaller as compared to the first set of samples. The decrease in the strength of the 5:1 compared to the 10:1 samples was expected, however it was hypothesized that the elongation at break would be increased. This wasn't necessarily the case and interestingly the MIX HPHU gave the highest elongation at break, where previously it was the lowest. Overall, this set has unsatisfactory results as similar properties are observed in sample No. 1 which has no A-POSS.

Finally, the third set of samples with a 10:1 ratio of IPTMS and using Jeffamine D-4000, gave the highest elongations at break and good tensile strength. The increase in elongation can be attributed to the longer chain diamine, Jeffamine D4000, which was the objective of using this. Very good tensile strength was also observed for this set and there was again an increase from the PHU to the HPHUs showing that the A-POSS is adding strength to the polymer network. Sample No. 9: MIX HPHU had the second highest elongation at break and the highest tensile strength of all the samples making it the best performing HPHU with a good mix between strength and

elasticity. When comparing this to ADFASTs PU, the tensile strength is doubled and the elongation at break falls well within the bounds, albeit on the lower end. Manipulating this formula by using a slightly lower IPTMS concentration (for example, 8:1 IPTMS:PHU), would likely give even higher elongations at break without sacrificing too much tensile strength. Overall, as it stands sample No.9: MIX HPHU is an excellent candidate to be able to replace the standard PU formulation for sealant applications based on mechanical properties.

Table 13: Tensile Testing Results

Set	No.	Ratio/Diamine	Sample	Youngs Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
	0	-	ADFAST PU	-	0.6 ± 0.2	60 ± 25
1	1	10:1 Jeff 2000	PHU	2.44	0.66	24.8
	2		TOP HPHU	3.72	1.17	28.2
	3		MIX HPHU	5.91	1.09	16.5
2	4	5:1 Jeff 2000	PHU	1.66	0.55	29.6
	5		TOP HPHU	2.43	0.76	28.1
	6		MIX HPHU	2.58	0.91	32.8
3	7	10:1 Jeff 4000	PHU	2.01	0.82	36.4
	8		TOP HPHU	1.66	0.84	46.1
	9		MIX HPHU	3.10	1.32	41.6

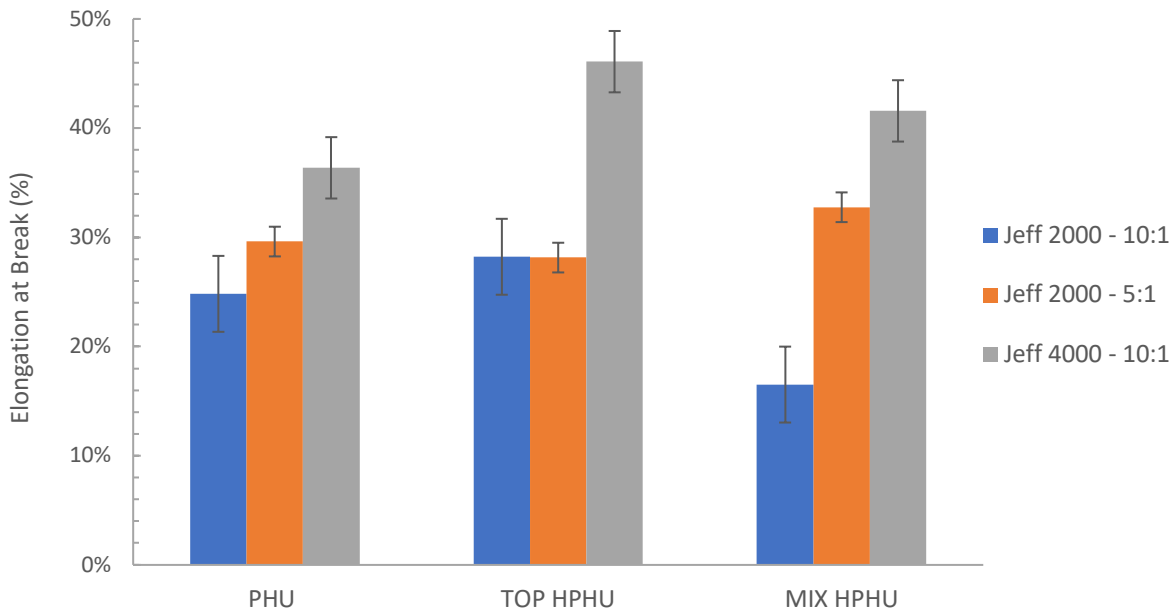


Figure 32: Elongation at Break of tested PHUs and HPHUs

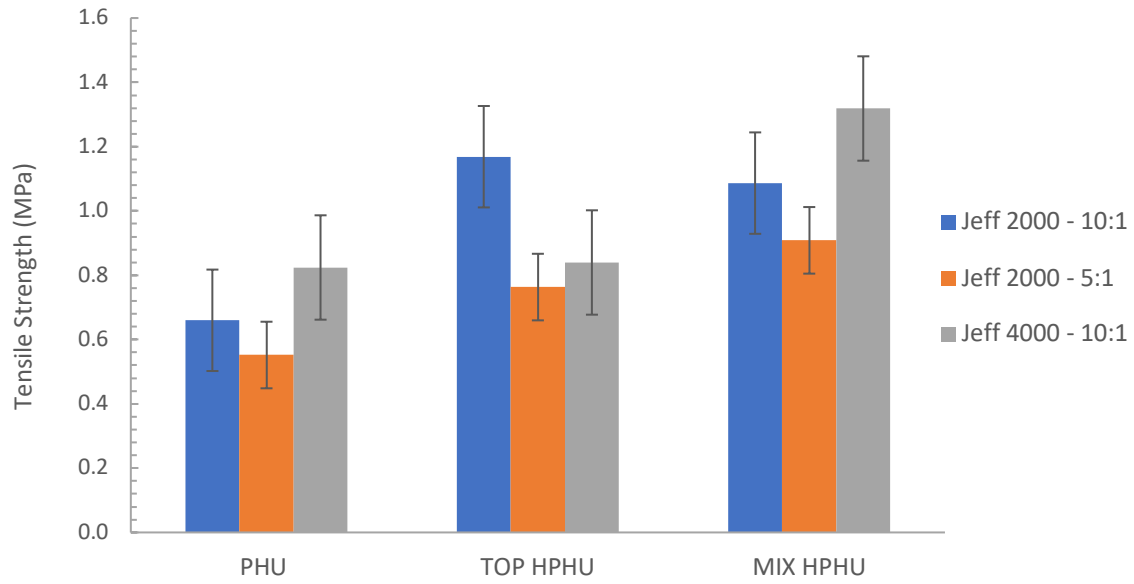


Figure 33: Tensile Strength of tested PHUs and HPHUs

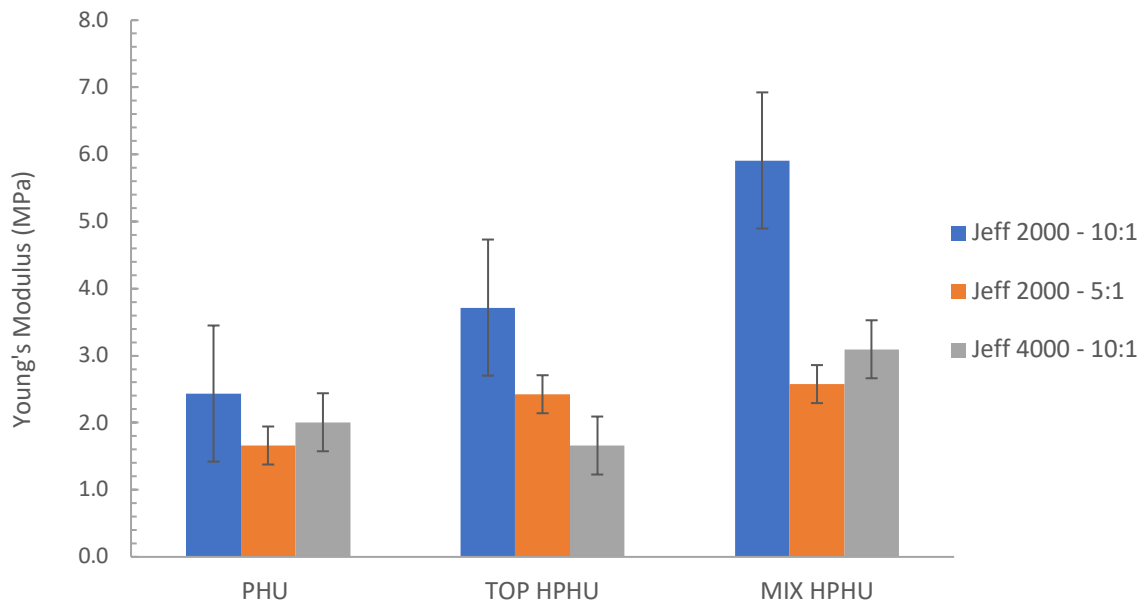


Figure 34: Young's Modulus of tested PHUs and HPHUs

4.3.2.7 Contact Angle Results

Next, contact angle testing was performed on sets 1 and 2 of the cured HPHUs. This test gives insight on the hydrophobicity of the films and shows how water interacts on the films surface. In general, the higher the contact angle, the more hydrophobic the sample is and the lower the contact angle, the more hydrophilic the sample. Contact angles above 90° are considered hydrophobic. Understandably, materials that are used for sealant applications are required to be hydrophobic as their main purpose is to seal objects to prevent water and moisture from passing through. Because of this, there are studies in which the goal is to increase the hydrophobicity of materials to make them more suitable for sealant applications [62].

Figure 35 shows an example of the contact angle measurement that was taken for one sample. A live camera is recording and once the droplet is dispersed onto the film a screenshot is taken to be able to measure the angles before the drop disperses. The software can detect the droplet and from there the left and right angles are reported. Each sample was tested at 5 different locations on the film and the results were averaged to give a single mean value for the contact angle. **Table 14** gives a summary of these results. Sample No.1: PHU-IPTMS-7 gave the lowest contact angle at 72.6° and the two HPHUs in the set both gave higher contact angles above 90° . The second set gave slightly lower angles, but an increase between the PHU and HPHU was still observed. Besides the first sample, all films were or very close to 90° , thus making them slightly hydrophobic. These results also confer with the gel content tests in THF and water and toluene swelling that was completed (**Table 9** and **Table 10**) as this shows that the addition of A-POSS increases the hydrophobicity of the polymer.

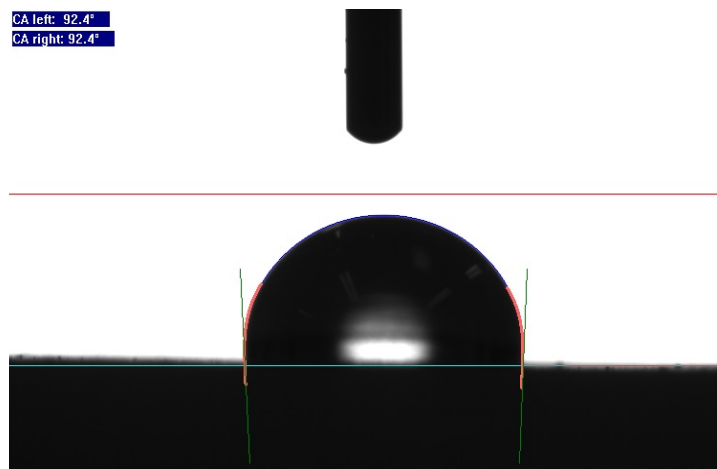


Figure 35: Contact angle measurement example

Table 14: Contact Angle Results

Set	No.	Ratio/Diamine	Sample	Contact Angle (°)
1	1	Jeff 2000 – 10:1	PHU-IPTMS-7	72.6
	2		A3.20-TOP-IPTMS	91.9
	3		A3.20-MIX-IPTMS	90.1
	7		4K-PHU-IPTMS	87.0
2	8	Jeff 4000 – 10:1	A4.2-TOP-IPTMS	89.2
	9		A4.1-MIX-IPTMS	87.2

5.0 CONCLUSIONS AND FUTURE WORK

The main objective of this thesis was to formulate a POSS-modified HPHU material that had improved mechanical and thermal properties compared to its PHU counterpart and was also comparable to typical PU sealants. To do this, PHU prepolymers were first synthesized and fully characterized to establish a benchmark. These prepolymers possessed CC end groups which were functionalized with an amino POSS (A-POSS) to end-cap the polymer and obtain a HPHU resin. This comprised the bulk of the work for this thesis and careful attention was directed towards ensuring POSS was covalently bonded to the polymer and not just mixed as an additive. Using FTIR, GPC, and NMR analysis, it was concluded that the A-POSS was successfully incorporated, and a hybrid polyurethane was synthesized without the use of isocyanates. The uncured HPHUs exhibited improved thermal degradation temperatures with increasing POSS concentration compared to their PHU counterparts. However, the HPHU T_g values for the cured polymers remained relatively similar to the cured PHU polymers.

The next step in this work was further functionalizing the HPHU resin with moisture curable moieties to allow the polymer to cure in ambient conditions. Since the polymer was already end-capped with POSS, the pendant primary and secondary hydroxyl groups in the backbone of the polymer were leveraged for this curing reaction. An isocyanate-functional silane was used to cap the pendant hydroxyl groups to obtain a final cured film. Overall, three sets of experiments, each with three reactions (totaling nine samples), were investigated in this step. Each set included the PHU prepolymer, the TOP HPHU, which was purified from excess POSS, and MIX HPHU, which had unreacted POSS left in the mixture. The first set of experiments used Jeffamine D-2000 as the diamine in the backbone of the polymer with a ratio 10:1 IPTMS:HPHU. The second set also used Jeffamine D-2000, but with a 5:1 ratio of IPTMS:HPHU. Finally, the third set that was explored used Jeffamine D-4000 as the diamine with a 10:1 ratio of IPTMS:HPHU. It was found that the MIX HPHU in the last set, using the longer chain Jeffamine D-4000, gave optimal results as a balance between strength and flexibility was achieved. FTIR confirmed the successful incorporation of the IPTMS into the HPHUs with no unreacted isocyanates left in the films. Furthermore, gel content, water and toluene swelling, and contact angle tests all showed improved crosslink density and hydrophobicity of the POSS-modified HPHUs compared to previously reported PHUs. Finally, the thermal properties of the cured films were only slightly improved, but significant improvements in the mechanical properties were observed. When compared to a typical

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PU sealant, the HPHU exhibited a tensile strength at break that was two-fold and a comparable elongation at break. The viscosity of the HPHU was also similar to the reference PU making it a suitable candidate for scale up. Overall, a successful HPHU polymer was synthesized, and it displayed favourable properties when compared to both the PHU prepolymers and typical PUs.

However, it is important to discuss and point out the obvious drawback that was presented in this work. Though a HPHU was successfully synthesized without the use of isocyanates, in the subsequent curing reaction, an isocyanate-functional silane was introduced. It is ironic that in the pursuit to obtain a curable HPHU film, an isocyanate was added to a NIPU formulation. The main reason for using the isocyanate silane was that it utilized the pendant -OH groups in the backbone of the polymer, which in turn increased the hydrophobicity. Furthermore, this forms additional urethane bonds, which increase the hydrogen bonding, strength, and adhesion. Finally, the reaction between isocyanates and hydroxyl groups is relatively quick and easy. Though an isocyanate was used in this formulation, the maximum amount used never exceeded 3 mL or 19 wt%. This is still a drastic reduction compared to conventional PUs, which use isocyanate as one of the main monomers and often in excess.

Overall, this method of incorporating silane end-cappers into the backbone of the polymer proved to be successful and tunable properties can be achieved. This leads to the future work that can be done to further improve the HPHU formulation. Specifically, research into finding a non-isocyanate silane end-capper that is compatible with hydroxyl groups would be the next step. A carboxylic acid-functional silane could be a good candidate as carboxylic acids and hydroxyls readily react to form ester bonds. Though there are not many commercially available products of this type, a recent study was able to synthesize carboxylic acid-functionalized silica particles by a co-condensation approach [63]. If suitable, this could be an interesting approach that would eliminate all isocyanates and thus form a true hybrid NIPU.

In addition to investigating different silane end-cappers without the use of isocyanates, there are a few alternatives that could be explored for the HPHU synthesis as well. First, would be investigating alternative silica materials that could be added to replace POSS to give a more cost-effective product. There are several different silane molecules that can be utilized, and future work could be dedicated to finding the optimal formulation that gives added strength without compromising on flexibility. Particularly, there are several commercially available fumed silicas with amino functionality that could be used, as well as a wide variety of silane coupling agents

available [64]. Additionally, the epoxy POSS that was initially investigated could be revisited now that a basis for adding POSS into the polymer network has been formed. This epoxy POSS could be carbonated and used as a branching agent for the PHUs to give a cross-linked network connected by POSS cages. This method could lead to a cured polymer without the need for a second silane agent added into the backbone of the polymer, which could make it an attractive approach. Finally, different diamines could also be investigated as this thesis presented how different chain diamines can affect the final properties. For example, a shorter chain diamine, such as Jeffamine D-403, could be explored for comparison to the longer chain diamines. Alternatively, an amino-functional silicone, such as NH_2 functional PDMS, could also be explored to examine the effects of incorporating silicone into the backbone of the polymer.

Overall, there is a wide variety of options to be able to further optimize the HPHUs presented in this work. Nonetheless, this thesis presented a novel and unique approach to obtain HPHU films and can serve as the basis for future formulations to be synthesized this way. The work in this field is very promising, and future outlooks seem optimistic to eliminate the dependence on isocyanates for PU formulations.

NOMENCLATURE

BADGE: Bisphenol-A Diglycidyl Ether, 8	IPDI: Isophorone Diisocyanate, 60
BDA: Butanediamine, 10	IPTMS: 3-Isocyanatopropyl(trimethoxy)silane, i, 22
CBMA: Cyclohexanedimethanamine, 14	M _c : Molecular Weight Between Crosslinks, 12
CC: Cyclic Carbonate, 3	MDI: Methylene Diphenyl Diisocyanate, 1
CDCl ₃ : Deuterated Chloroform, 22	M _n : Average Molecular Weight, 26
CMR: Carcinogen, Mutagen, and Reprotoxic, 1	M _w : Weight Average Molecular Weight, 26
Đ: Dispersity, 26	mXDA: m-Xylyene Diamine, 10
DAMO: N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 22	NIPU: Non-Isocyanate Polyurethanes, 1
DDA: Dimer Diamine, 10	NMR: Nuclear Magnetic Resonance, 26
DDM: Diaminodiphenyl Methane, 13	PACM: 4,4'-methylenbis (cyclohexylamine), 11
DDSQ: Double Decker Silsesquioxane, 19	PDMS: Poly(dimethylsiloxane), 20
DGC: Diglycerol Dicarboxate, 4	PGTE: Phloroglucinol Tris-Epoxy, 8
DIG: Diglycerol, 22	PHU: Polyhydroxyurethane, 3
DMC: Dimethyl Carbonate, 22	POSS: Polyhedral Oligomeric Silsesquioxane, 5, 13, 16, 17, 19, 22
DMF: Dimethyl Formamide, 22	PPG: Poly(propylene glycol), 20, 22
DMSO- <i>d</i> ₆ : Deuterated Dimethyl Sulfoxide, 22	PU: Polyurethane, 1
DSC: Differential Scanning Calorimetry, 27	RO: Reverse Osmosis, 22
DYTEKA: 2-methylpentane-1,5-diamine, 14	SOM: Sodium Methoxide, 22
E: Young's Modulus, 58	TBD: 1,5,7-Triazabicyclo[4.4.0]dec-5-ene, 22
EB%: Elongation at Break, 58	TCI: Tokyo Chemical Industry, 22
EDA: Ethylenediamine, 8	T _d : Thermal Degradation Temperature, 16
FDA: Fatty Acid Diamine, 10	T _{d,onset} : Onset Degradation Temperature, 46
FTIR: Fourier Transfer Infrared, 26	TDI: Toluene Diisocyanate, 1
G'': Loss Modulus, 54	TETA: Triethylenetetramine, 6
G': Storage Modulus, 54	T _g : Glass Transition Temperature, 8
HMBC: Heteronuclear Multiple Bond Correlation, 27	TGA: Thermogravimetric Analysis, 27
HMDA: Hexamethylenediamine, 17	THF: Tetrahydrofuran, 22
HUM: Hydroxyurethane Modifiers, 6	T _m : Melting Temperature, 46
IDM: Internal Dispersion Monomer, 10	TMPTGE: Trimethylpropane Triglycidyl Ether, 11
IPDA: Isophoronediamine, 13, 17	σ _{max} : Tensile Strength, 58

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APPENDIX A: IPTMS RATIO CALCULATION

To determine how much IPTMS was required for the curing reactions, the absolute molecular weights were required. Similar to the calculation given in section 4.1.1, the IPTMS ratio was found by the following example calculations:

- The average number molecular weight, M_n , of DGC-PHU-11 from GPC data is:

$$M_n = 5,900 \text{ g/mol}$$

- The average number molecular weight of Jeffamine D-2000 from GPC data is:

$$M_n = 1,800 \text{ g/mol}$$

- Dividing the molecular weight of DGC-PHU-11 by Jeffamine D-2000 gives the number of diamine molecules in the prepolymer chain:

$$5,900 / 1,800 = 3.28 \approx 3$$

- Thus, each PHU chain has 3 Jeffamine units, which are separated and end-capped by DGC (as further confirmed by FTIR and ^1H NMR), giving 4 DGC units. Knowing the absolute molecular weight of DGC is 218 g/mol and Jeffamine D-2000 is 2000 g/mol, the absolute average number molecular weight of DGC-PHU-11 is:

$$M_n^{\text{absolute}} = (3 \times 2000) + (4 \times 218) = 6,872 \text{ g/mol}$$

- As shown in **Scheme 7**, there are two hydroxyl groups that are formed for each Jeffamine and DGC bond, therefore:

$$(2 \text{ OH groups}) \times (3 \text{ Jeffamine units}) = 6$$

$$6 + 2 \text{ OH groups (formed on each end of the CCs)} = 8 \text{ OH groups total}$$

- Finally, when the A-POSS is added onto the end of the polymer, this creates 2 additional OH groups, one on each end:

$$(8 \text{ OH groups}) + (2 \text{ OH groups}) = 10 \text{ OH groups total}$$

- Therefore, a maximum ratio of 10:1 of IPTMS:HPHU was required to cap all the OH groups that are formed in the HPHU synthesis.