THE UTILIZATION OF BARK TO MAKE RIGID POLYURETHANE FOAMS

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Faculty of Forestry
University of Toronto

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Abstract

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This work focused on the characterization of polyols derived from the liquefaction or alkoxylation of bark. Regarding liquefaction, it was found that both temperature and solvent structure played a significant role in polyol properties. High temperature liquefaction resulted in the degradation of sugars, while liquefaction at mild temperatures preserved sugar structures as shown by $^{31}$P-NMR. It was also shown that liquefaction at 130 °C was ideal in terms of producing a polyol with a relatively flat, broad, plateau of molecular weight distribution, whereas liquefaction at 90 and 160 °C produced polyols with a large amount of low molecular weight compounds. Regarding solvent structure, it was found that polyhydric alcohols with short chain primary hydroxyls resulted in less sugar degradation products and less formation of condensation side-products. It is proposed that the highly polar environment promoted grafting and prevented condensation onto other biopolymers. Using organic solvents it was found that ketonic solvents like acetyl acetone and cyclohexanone, through their highly polar carbonyl group could engage in hydrogen bonding through electron donation/proton accepting interactions. These enabled the solvent to reduce the amount of condensation reactions and improve liquefaction yield. The liquefied bark-based polyols were then used to make polyurethane foams. It was found that when a diversity of hydroxyl groups were present the foaming rate was reduced and this may reflect a slower rate of curing and explain why the bark foams had a greater amount of cells that underwent coalescence. It was also observed that the bark foams had a low amount of closed-cell content. Since closed-cell content plays a role in dictating elastic compression, this may explain why the bark foams exhibited a lower elastic modulus. Finally, as a contrast to liquefaction, bark was alkoxylated. It was observed that the conversion yield was higher than liquefaction. The polyols had a high average molecular weight with a broad distribution and far greater solubility. It is proposed that alkoxylation is far less degradative than liquefaction. This may explain why the foams showed improved compressive behaviour compared to the foams made from liquefied bark-based polyols. Through greater characterization of the structure of polyols produced via liquefaction and alkoxylation the relationships between reaction parameters, polyol structure, and foam properties can be better understood. This is an important step towards the utilization of bark to make polyurethane foams.
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List of Abbreviations

AA acetyl acetone
AISL acid-insoluble lignin
CB chlorobenzene
CFC chlorofluoro hydrocarbons
CH cyclohexanone
CT condensed tannins
DMA dynamic mechanical analysis
DMC double metal cyanide catalyst
DMP 2,4-dimethylepentanone
DP degree of polymerization
DTG derivative thermogravimetric analysis
EO ethylene oxide
FTIR Fourier Transformed Infrared
GPC gel-permeation chromatography
HCFC halogenated chlorofluoro hydrocarbons
HMDI hexamethylene diisocyanate
HT hydrolyzable tannins
ICI isocyanate index
LMW low molecular weight
MDI methylenediphenyl isocyanate
MW molecular weight
NMR nuclear magnetic resonance
OHV hydroxyl value
OP-AB  oxypropylated alkaline bark
OP-B  oxypropylated bark
PAC  proanthocyanidins
PC  procyanidins
PD  prodelphinidins
PEG  polyethylene glycol
PF  phenol-formaldehyde
PO  propylene oxide
PPG  polypropylene glycol
PU  polyurethane
PUF  Polyurethane Foam
TDI  toluene diisocyanate
TEDA  triethylenediamine
TGA  thermal gravimetric analysis
TMDP  2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane
Chapter 1

Introduction

“Societies become great when old men and women plant trees who’s shade they know they will never enjoy”, according to a greek proverb. This proverb seems apt, it is about building for the future, and that future relies on trees. Building for the future requires sustainable development, and this research is on developing sustainably sourced materials. Although there are many exciting avenues of research leading to this broad goal, the path to be explored in this work is the utilization of bark to produce polyurethane foams. There are a couple reasons why this project can be considered a route towards sustainability. Firstly, polyurethane foams are traditionally made from petrochemicals. It is the hope of this project that some of that petrochemical component could be substituted with chemicals derived from natural materials. This would help replace a dwindling resource with one that is renewable. Secondly, bark is a waste material produced by at sawmills that is often burnt in boilers or used in other low value applications like mulch or animal bedding. For example, the mountain pine beetle infestation in British Columbia as shown in Figure 1.1a has devastated over 710 million cubic meters of waste timber and bark, providing a large surplus of this feedstock to be utilized.[1] This is contrary to plant oil-based foams that are derived from agricultural food crops. The ramifications of this is threefold since utilization of these crops can cause the price of foods to rise, food crops for sustenance could be replaced with cash crops, and as land usage shifts towards agricultural uses a greater amount of deforestation will occur. Therefore the utilization of bark does not come with the social and environmental issues associated with plant-oil alternatives. Lastly, polyurethane foams can be an excellent form of insulation. Although commonly used in commercial and industrial buildings, it could be envisioned that a less expensive polyurethane could encroach upon the residential sector, and bestow a lower energy footprint through improved insulation. For these reasons bark shows potential to be a sustainable feedstock.

Aside from the social and environmental reasons there are three technical reasons for pursuing research on bark. Firstly, the highly recalcitrant nature of the lignin matrix and crystalline cellulose has been a barrier to the utilization of many types of biomass since harsh experimental conditions are needed as shown in Figure 1.1b. However, bark has a high fraction of extractive compounds, aptly named due to their small molecular weight that makes their extraction quite easy. Secondly, many of the compounds found in bark have a high degree of hydroxyl functionality (important for the reaction to produce a polyurethane). Thirdly, they also contain aromatic groups as shown in Figure 1.1c. Aromatic groups can impart thermal stability to the polyurethane. These aspects will be discussed further in the literature review.
Figure 1.1: a) The pine beetle and its damage to the forests of British Columbia, contrasted to the deforestation in the Amazon due to soya plantations; b) the lignocellulosic matrix of highly recalcitrant lignin and crystalline cellulose; c) some bark tannins that have hydroxyl functionality and aromatic groups[2]
1.1 Statement of the problem and purpose of the study:

Although bark may seem appealing, the feasibility of its utilization is far from straight forward. Bark is a highly complex material. It consists of many different biopolymers, it varies between the different structural layers of bark, between species, is affected by environmental conditions, and lastly how it is treated once stripped from the log. With all this variation and complexity how does one convert bark into a form that is suitable for making a polyurethane? How does all this variation manifest itself in terms of polyol characteristics? Finally, how does the incorporation of a bark-based polyol affect the polyurethane foam properties?

In this study two thermochemical treatments of bark known as liquefaction and alkoxylation will be evaluated. These methods convert bark into a liquid polyol, a viscous solution rich with reactive hydroxyl groups. These thermochemical treatments convert a highly complex solid into a homogenized liquid. There are many criteria that a polyol must have, such as a suitable range for the hydroxyl content, viscosity, and molecular weight. Aside from these traditional aspects of polyol properties, polyol characterization is also essential to understanding how reaction parameters alter the bark biopolymers. The bark biopolymers can be cleaved, grafted, undergo condensation onto other biopolymers and have functional groups oxidize. Therefore polyol characterization is key to understanding the mechanisms of conversion, but also for understanding how to tune the structure of the polyol to ensure compatibility in a rigid foam formulation. Foams will be studied to a lesser extent, only as a means to understand how polyol structure impacts foam properties. In summary, the main purpose of this study is to assess the suitability of bark as a feedstock for making a polyol by understanding how liquefaction and alkoxylation impact the characteristics of a polyol.

1.2 Research Goals

The broad goal of this research is to better understand how the conversion processes impact bark-polyol structure. This goal has been broken down into more specific research goals:

- To understand how liquefaction temperature impacts polyol structure and the extent of biopolymer degradation.
- To understand how liquefaction solvent structure (polyhydric alcohols/organic aprotic solvents) affect polyol composition and degradation.
- To understand how liquefied bark-based polyols impact the properties of the polyurethane foams.
- To understand how the alkoxylation of bark contrasts to liquefaction, in terms of both the structure of the polyol and the foams.

1.3 Thesis Statement

The utilization of bark-based polyols depends upon a thorough understanding of the structure and properties of the polyol. It is proposed that by contrasting the methods of conversion, altering reaction parameters, and connecting polyol structure to foam properties, that the structure of the polyol will be better understood, the polyol can be improved in quality, and a truer assessment of the potential of bark-based polyols can be made.
1.4 Hypotheses

- Conversion yield and foam properties are often the focus of many papers on liquefaction. A higher liquefaction temperature is often used to achieve a greater conversion yield, but it is unknown how this impacts the polyol structure. **It is proposed that by varying the liquefaction temperature that the amount of degradation will vary, as well as key polyol characteristics.** By characterizing how the polyol changes with temperature, the quality of the polyol can be improved.

- Since studies on liquefaction have focused on conversion yield and foam properties little is known about the interactions between solvents and the biomass. **It is proposed that by varying the structure of various polyhydric alcohols and organic solvents that their influence on polyol composition and extent of degradation can be better understood.** By understanding the interaction of the solvent with the bark it will enable solvent selection to be an additional parameter by which the quality of the polyol may be improved.

- The above work has shown that bark-based polyols have hydroxyl values and viscosities within the typical range used for rigid foams. However, the above characterization revealed other polyol characteristics that differed, like the type of hydroxyls present, the broad molecular weight range, and the presence of degradation compounds. **It is proposed that these differences in the polyol will result in significant changes to the foaming behaviour and foam properties.** By understanding how the presence of bark compounds in the polyol influences foam properties, new insights can be made about the polyol’s structure and lead to new considerations for polyol design.

- Liquefaction is a process that relies on chain cleavage under acidic conditions, whereas alkoxylation is inherently a derivitization reaction. However, a material like bark or alkaline extracts of bark have hitherto not been alkoxylated. Therefore it is unknown how bark biopolymers and bark’s ultrastructure will respond to the solvent-less, high pressure, basic conditions of an alkoxylation reaction. **It is proposed that alkoxylation will result in less degradation, and will show improved polyol/foam properties.**

1.5 Outline

There is a rich body of literature that is the foundation of this research. In chapter 2 the following questions are answered: What is the structure and composition of bark? - What are the characteristics of a typical polyol? - How do biomass conversion techniques convert biomass into a polyol? - and lastly, How would a biomass-based polyol behave in a polyurethane foam? This work hopes to build upon and contribute towards this body of literature by identifying gaps in this knowledge base. Many of the gaps in understanding relate to a lack of in depth characterization of the polyol. For this reason the focus of this work has been on characterization of the polyol. The various characterization methods utilized have been detailed in chapter 3.

The research conducted on the characterization of bark-based polyols is detailed in the following four chapters. In chapter 4 the liquefaction temperature is varied to see how this impacts polyol structure and the extent of biopolymer degradation. Continuing the work on liquefaction in chapter 5, the effect of
solvent structure (polyhydric alcohols/organic aprotic solvents) on polyol composition and degradation was examined. To conclude the work on liquefaction, in chapter 6 the effect of liquefied bark-based polyols on the properties of the polyurethane foam was examined. Finally, in chapter 7 bark underwent alkoxylation, and the structure of the polyol and the foam were contrasted to the previous results from liquefaction. Finally, the main conclusions from this work are summarized in chapter 8 and future work is briefly discussed in chapter 9.
Chapter 2

Literature Review

2.1 Bark

Bark has been utilized by society for many purposes throughout history. In some applications it is harvested on an industrial scale, in others it remains a niche market. Historically, tannins from bark were used in the tanning of leather and bark was used to waterproof canoes built by indigenous peoples. Currently, most of its use is as boiler fuel at pulp and paper mills and as mulch. Certain species of trees have bark with more unique applications like cinnamon that is used to add flavour and spice to our foods, while cork is used to build insulating and dampening materials. Paclitaxel (Taxol) is a bark extract from Pacific Yew, and is an approved chemo-therapy medicine for treating breast and ovarian cancer. Its structure was used as inspiration for a synthetic version. These varied applications should highlight the fact that bark is a highly diverse material with structure and composition varying from species to species. Some of this variation is evident from Figure 2.1, where the thorny appearance of honey locust bark can be compared to the smooth papery texture of Birch bark and to the rough flaky appearance of lodgepole pine bark. This variation is because bark serves a variety of natural purposes.

Figure 2.1: The variation in bark is evident from the a) thorny appearance of honey locust bark, b) the paper like appearance of birch bark, and the flaky appearance of lodgepole pine bark.

Before going into further discussion about the utilization of bark compounds it may be useful to gain an appreciation for bark’s natural role, its growth and life-cycle, and structure. Bark has a protective role as it shields a tree from physical and biological threats like weather (heat, hail, frost, UV), insects, birds, mammals, parasitic plants, fungi, and bacteria.[3] Part of this defence against infection is achieved through the polyphenolic compounds in the bark that have anti-fungal and anti-microbial properties. It can serve as a storage area, pines store resin; elms store mucilage (glycoproteins); oaks, birch, willow, and spruce store tannins; basswood and beeches store inorganic crystals of calcium oxalate or silicates.[3] Bark also has a very important role in nutrient transport, as the phloem is used to move sap in the spring upwards towards the crown and in the fall moves photosynthesis products from the crown towards the roots for storage. Finally, bark also serves an important role in acting as a moisture barrier, using waxy compounds like suberin help the sap wood to retain moisture. It is clear from looking at the various functions of bark that these different roles require different structures, bark actually constitutes a series of layers with distinct functions and composition.

2.1.1 Structure and morphology

The different structural features of bark are shown in Figure 2.2. From the center of a tree’s trunk there is the pith; then the heartwood; followed by the sapwood (xylem); then the vascular cambium, that contains meristematic cells for growth of new wood. The vascular cambium produces xylem on the woody side and phloem on the bark side. Bark is sometimes delineated into a physiologically active area called the inner bark and an inert outer layer called the outer bark. Inner bark (or phloem) has three main cellular structures with the following functions: sap transport through thin-cell walled sieve elements (3-4 mm), storage in parenchyma cells (1/10 mm), and mechanical strength through sclereid or bast fibers (1.5 mm).[2, 4]

Sandwiched between the inner bark and outer bark is the cork cambium (phellogen), which contains meristematic cells and is where growth occurs. On the inner bark side phelloderm is produced, on the outer bark side cork (phellem) is made. The cork (phellem) side is typically rich in suberin, its waxy nature ensures moisture retention, but also inhibits infection. As a tree ages a new cork cambium layer will form within the phloem layer, and some of the phloem and old periderm (phelloderm, phellogen, phellem) will be pushed outwards to form a dead layer.[3] These dead layers of phloem and periderm make up the outer bark. As the trunk grows and expands outwards the outer bark is compressed on the inside and has internal tension near the outer edges, eventually leading to tears. As the tree ages the outer bark continues to crack, flake or peel (depending on species) and this is what produces the characteristic roughened appearance and texture of bark. Another key feature of bark are lenticels, these are porous structures on the bark that enable gases produced from metabolism to be transported through the bark from the living tissues to be released outwards.

In this work, both inner and outer bark were utilized of lodgepole pine. Although bark has some generalities in terms of structure; the thickness, mass amount, and morphology of these structures could vary greatly; and as a result variation between species in terms of accessibility to chemicals and composition could also vary greatly. Furthermore, the process of grinding bark does not produce a homogenous powder, only parenchyma and sieve cells will form a fine powder, but the bast fibers, cork cells stay relatively intact. Therefore, the relative ratio of these cells depending on species and the very process of sieving for a certain particle size may alter the composition of a bark-based material.[4] This demonstrates that species variation is likely a key factor in terms of the utility of bark. With some
species having bark that is perhaps highly suitable to thermochemical treatments and promising polyol properties, while bark from another species could behave differently. A discussion of the variation in composition and structures present in bark will be the focus of the following section.

Figure 2.2: The bark is shown in relation to the trunk of a tree, and in addition the key components in the inner and outer bark (Jason D’Souza)

2.1.2 Bark components and compositional variation among species

The chemical composition of bark is highly diverse in structures and in variation among species. However, bark does bear some resemblance to wood, especially the inner bark, due to many of the same biopolymers being present, like lignocellulosic components like the polysaccharides of cellulose and hemi-cellulose, and lignin. From Figure 2.3 it can be seen that bark tends to have a greater amount of lignin, extractives, and ash than wood; while wood has a greater fraction of polysaccharides. The chemical structure of extractives and the lignocellulose components will be discussed further in the following sections.

Extractives

This family of compounds is a very broad classification named simply for the fact that they can be easily leached from biomass. Typical solvents include aqueous sodium hydroxide solutions, simple alcohols, alkanes, benzene, diethyl ether, acetone. The general chemical structures of some of these compounds are shown in Figure 2.4. This vague definition means that composition of the extractive fraction will vary depending on the leaching conditions (i.e. solvent and temperature) and on the botanical origin (being highly species and tissue dependent). The extractive compounds most relevant to bark will be discussed. The variation in extractive contents depending on species and on extraction solvent can be seen from Figure 2.5. It is clear from this that lodgepole pine has the largest amount of sodium hydroxide and benzene extractives content. This is part of the rationale for utilizing this species of bark in this work. Furthermore, from Table 2.1 it can be seen that lots of these compounds are likely to be terpenes,
Figure 2.3: The typical variation in bark is clear from the crude comparison between wood and bark and between barks of softwoods vs. hardwoods. This exhaustive study was from a USDA report on bark.[2]

waxes, fatty acids and sugars. In a detailed study by Rowe et al. a more detailed examination of the benzene extracts was done and can be seen in Figure 2.6.[5] Thus it can be seen that a large amount of the extractive compounds are in fact various terpenoids and free acids (resin acids with structures like the diterpenes shown in Figure 2.4). Alcohol extractions however appear to extract a greater amount of tannins, and this showed that western larch, engelmann spruce, sugar pine, and eastern hemlock have a high tannin content.

Table 2.1: Dependence of extractives composition on solvent; adapted from a USDA report[2]

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Type of Extractive Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>petroleum ether, ether, benzene, chloroform</td>
<td>terpenes, fats, waxes, fatty and wax acids, sterols, resins</td>
</tr>
<tr>
<td>alcohol, acetone, aq. alcohol, aq. acetone</td>
<td>simple polyphenols and their glycosides, tannins, mono and disaccharides</td>
</tr>
<tr>
<td>hot/cold water</td>
<td>disaccharides, starch, gums, pectins, tannins, mucilages</td>
</tr>
<tr>
<td>aq. alkali</td>
<td>phlobaphenes, phenolic acids, lignin, hemi-cellulose, suberin</td>
</tr>
<tr>
<td>acid hydrolysis</td>
<td>sugars, uronic acids</td>
</tr>
</tbody>
</table>
Figure 2.4: Chemical structures of various extractive compounds found in bark
Chapter 2. Literature Review

Figure 2.5: The variation in bark is clear from the highly detailed species level comparison of bark extractives. This data was from a USDA report on bark.[2]
Tannins is a broad name for biomolecules that were historically used for the tanning of animal skins, but are also the compounds responsible for the distinctive flavours in wine, tea, and fruit juices.[6] They can be broken into two categories, hydrolyzable (HT) and condensed tannins (CT), whose structures can be seen in Figure 2.7. The HT have carbohydrate centers (ex. glucose) with the hydroxyl groups partially or totally esterfied with groups like gallic acid (gallotannins) or ellagic acid (ellagitannins). It is the labile ester bond that is broken when exposed to water that makes these hydrolyzable tannins easy to extract.

In contrast, CT are much more stable, and polymeric in nature. CT are now more commonly referred to as proanthocyanidins (PAC). The monomer unit belongs to a class of molecules known as flavan-3-ols. The physical and chemical properties are dependent on many factors of the molecular structure of PACs such as: molecular weight, type of interflavanoid linkage, and hydroxylation pattern.

PAC are polymers with up to 50 units depending on the plant species. The molecular weight (MW) or degree of polymerization (DP - number of monomer units) are important determinants of PAC solubility. Monomers, dimers and trimers will be soluble in an organic phase, whereas higher MW oligomers will prefer a water phase.[7] Although, with increasing MW the oligomers become less soluble and difficult to extract without the use of harsher extraction conditions (harsher conditions result in depolymerization of the PAC). The variation in DP is dependent on the source of the PAC as shown in Table 2.2. The characterization of PAC is quite difficult, but with new and improved characterization methods that fragment the polymers less, it is likely that previous work underestimated the DP. Newer work estimates pine tannins to have DPs of up to 16 units![8]

PACs primarily bond through methylene linkages at the 4,8 position, but can also form a 4,6 arrangement; both bonding arrangements are referred to as B-type PAC. PACs can also form the more extravagant A-type with two bonds linking the flavan-3-ols. This is worthy to mention since the type of linkages present can affect the supramolecular structure and therefore affect the depolymerization, solubility, and reactivity of the tannins.

The variation in hydroxylation can be seen in Figure 2.7. Although these variations exist, prodelphinidins (PD - OH groups at 3,3′,4′,5,5′,7) are the main constituent in leaves of conifers, flowers of...
Figure 2.7: The chemical structure of hydrolyzable tannins, showing their basic building blocks and condensed tannins showing the variation in polymer linkages and hydroxylation pattern.

Table 2.2: The degree of polymerization of tannins from various sources, as determined by matrix assisted laser desorption ionization time of flight mass spectrometry by Monagas et al.\cite{9}

<table>
<thead>
<tr>
<th>Source</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mimosa bark</td>
<td>2-4</td>
</tr>
<tr>
<td>Acacia auriculiformis bark</td>
<td>3-5</td>
</tr>
<tr>
<td>Pinus radiata bark</td>
<td>2-8</td>
</tr>
<tr>
<td>Pinus massoniana bark</td>
<td>2-13</td>
</tr>
<tr>
<td>Pinus pinaster bark</td>
<td>1-7</td>
</tr>
<tr>
<td>Cranberries</td>
<td>4-10</td>
</tr>
<tr>
<td>Grape skins</td>
<td>3-5</td>
</tr>
<tr>
<td>Pear Juice</td>
<td>3-23</td>
</tr>
<tr>
<td>Apples</td>
<td>2-15</td>
</tr>
</tbody>
</table>
gymnosperms and angiosperms, while procyanindins (PC - OH groups at 3,3',4',5,7) are the dominant type in bark.[10] This work is focused on bark, but it is important to realize that if other forms of biomass are used or species, that variation in the types of monomers and hydroxylation patterns is possible.

With regard to reactivity it is said that the A-ring is the primary determinant of the lability of the interfalvanoid bond and adhesive strength. For example, when the A-ring has OH substitutions at both 5 and 7 it is susceptible to bond cleavage in both acidic and basic reaction conditions. The B-ring is also similar in nature to phenol and undergoes many of the same reactions.[10] Under acidic conditions the heterocyclic ring (c-ring) can undergo cleavage to form a reactive p-hydroxy benzyl carbonium ion which can then react with the nucleophillic A-ring to form a high molecular weight condensation product called phlobaphenes. Since these tend to have very low solubility they tend to precipitate.

To summarize, tannins refer to a broad range of molecules with various configurations and molecular weights. The commonality between all these is the high number of phenolic alcohol groups. It is this feature that makes them ideal for utilization in PUFs. However, their natural structure will be altered through the extraction process and this will be discussed more in the section on biomass conversion methods.

Terpenoids are a highly diverse and broad category of compounds. They are based upon the isoprene unit, $C_5H_8$. With two double bonds, this monomer can react in a variety of ways, forming higher molecular weight polymers and also gaining a variety of functional groups through a variety of biosynthetic pathways. Monoterpenoids (10 carbon terpenoids) and sesquiterpenoids (15 C) are referred to as essential oils and are the volatile liquids that provide many of the natural fragrances from plants.[11] Some terpenoids have been found to have biological functions, like some sesquiterpenes are dormancy hormones (tell the tree to hibernate in the fall), while some diterpenoids (20 C) are growth hormones (tell the tree to start growing in the spring). The purpose of other terpenoids is not very clear, some serve as gums, resins, and saps, while others may simple be by-products of a biosynthetic pathway.[11]

Rowe et al. characterized the benzene extract (28.7 % yield with respect to oven dry bark) of lodgepole pine bark. Upon saponification of the extract (a treatment with strong base), the triglyceride waxes would be removed, while the unsaponifiable material (43 % of benzene extract) would be the terpenoid fraction. These terpenoids had a small fraction of low molecular weight sterol structures like B-sitosterol, but mainly was composed of higher terpenoids like epimanool. These structures can be seen in Figure 2.8, and it is clear that these compounds have low hydroxyl functionality, with usually just one secondary alcohol. Therefore, although bark has a high concentration of extractive-type compounds, the type of extractives is quite important! A high concentration of tannin like extractives would be better suited than terpenoids for making a polyol.
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Figure 2.8: The chemical structure of the terpenoid building block isoprene. Some terpenoids found in lodgepole pine bark: a volatile oil B-sitosterol, and the terpenoid with the highest concentration in the bark epimannol

**Suberin and Waxes** have three main functions in the bark all related to being a diffusion barrier. Firstly, it is deposited in the phellem or cork cells in the periderm to help the tree prevent moisture loss to the environment. Secondly, it lines idioblast cells; these are storage cells that contain various compounds like pigments and minerals. Finally, upon damage to the tree, the wound is quickly suberized to prevent infection.[11]

The moisture barrier behaviour of suberin is due to its phenolic and aliphatic components that make it highly hydrophobic, as is evident from the model structure shown in Figure 2.9. For example, Douglas Fir bark suberin upon saponification (treatment with base) yields 43\% phenolic acids and 35\% aliphatic acids.[11] The aliphatic component consists of ester linkages. When depolymerized this yields Ω-hydroxy acids (hydroxyl is on the farthest carbon from the carboxylic acid) and dicarboxylic acids, with chain lengths ranging from 16-28 carbons depending on species.[11] Therefore it can be seen quite clearly, that the very long waxy chains and the phenolic compounds in suberin can yield a high amount of polymers containing carboxylic acids. This is of relevance since the reactivity of carboxylic acids with isocyanate differs from alcohols, and also the waxy nature of the compounds may influence foam cell stabilization.

Figure 2.9: A model molecular structure of suberin[11]
Cellulose

Cellulose on the molecular level is a linear polymer of D-glucose sugar units linked by $\beta$-1,4 linkages as shown in Figure 2.10. The $\beta$-1,4 linkage results in a 120° bond angle that produces long linear chains that enable intra-molecular bonds between O-3-H to O-5' and O-2-H to O-6'; and intermolecular bonds between O-6-H and O-3 of a neighbouring chain as shown in Figure 2.11a.\[12\] However, cellulose comes in a range of DP (<12000 from cotton and wood pulp from 600-1200) and polydispersity depending on plant species, origin, and processing.\[12\] These variations interrupt the perfection of the crystallites leading to amorphous regions. This two-phase model can be imagined as the 'fringed fibril model' depicted in Figure 2.10b

Figure 2.10: a) Chemical structure of various sugars and the polysaccharides they form
Chapter 2. Literature Review

Hemi-cellulose

This polysaccharide is a branched polymer as shown in Figure 2.10; being composed of different sugar units (of both pentose and hexose type: D-xylose, D-mannose, D-galactose, D-glucose, L-arabinose, 4-O-methyl-glucuronic, D-galacturonic and D-glucuronic acids), with primarily $\beta$-1,4 linkages but also $\beta$-1,3 bonds.\[13\] One more difference between hemi-cellulose and cellulose is the significantly shorter DP that ranges from 100 - 200.\[14\] Hemi-cellulose is more susceptible to hydrolysis because it does not aggregate into crystallites like cellulose and is consequently more accessible and more easily cleaved. It was shown by Fencel et al. that the type of sugar actually affects the yield of hydrolysis, and that yields of xylose were the highest, while arabinose and glucose were more resistant.\[15\] The details of how polysaccharides behave under the conditions of liquefaction will be discussed in later sections. Additionally, it should be noted here that all these polysaccharides have a high degree of hydroxyl functionality as either primary or secondary alcohols. Thus polysaccharides have some potential for being used as a polyol.

In Figure 2.12 the sugar content of various types of bark can be found, and in Figure 2.13 the sugar content is broken down into its monosaccharide content. Just within pine species it can be seen that sugar content ranges from 22-42 % and that when broken down into the monosaccharide content lodgepole Pine has the lowest amount of glucose at 50 %. An implication of this low glucose content is that the polysaccharide fraction consists of hemi-celluloses that are more susceptible to conversion into a polyol. In contrast, a bark like American elm with upwards of 70 % glucose content is more likely to have that glucose forming crystalline cellulose, that would hinder conversion into a polyol.

This discussion of the polysaccharides has shown how the sugar structure, molecular weight, the types of bonds, and branching can dictate the supramolecular properties, like the accessibility to solvent. The ability to liquefy polysaccharides into a polyol requires cleavage of bonds throughout the hierarchical structure to achieve a high yield. One of the greatest barriers to this is lignin.
Reducing sugars produced by hydrolysis of bark with 72 percent sulfuric acid
(Percentage as glucose, based on weight of oven dry, unextracted bark)

<table>
<thead>
<tr>
<th>Species</th>
<th>Unextracted bark</th>
<th>Extractive-free bark</th>
<th>Alkali-extracted bark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fir, balsam</td>
<td>46.6</td>
<td>45.3</td>
<td>32.9</td>
</tr>
<tr>
<td>Larch, western</td>
<td>46.6</td>
<td>46.0</td>
<td>38.0</td>
</tr>
<tr>
<td>Spruce, Engelmann</td>
<td>42.9</td>
<td>34.3</td>
<td>24.2</td>
</tr>
<tr>
<td>Spruce, black</td>
<td>47.9</td>
<td>44.8</td>
<td>32.3</td>
</tr>
<tr>
<td>Pine, jack</td>
<td>30.6</td>
<td>28.8</td>
<td>21.1</td>
</tr>
<tr>
<td>Pine, lodgepole</td>
<td>38.3</td>
<td>32.9</td>
<td>19.2</td>
</tr>
<tr>
<td>Pine, slash</td>
<td>29.7</td>
<td>29.8</td>
<td>26.4</td>
</tr>
<tr>
<td>Pine, sugar</td>
<td>22.1</td>
<td>19.8</td>
<td>16.1</td>
</tr>
<tr>
<td>Pine, western white</td>
<td>42.6</td>
<td>34.0</td>
<td>26.0</td>
</tr>
<tr>
<td>Hemlock, eastern</td>
<td>34.9</td>
<td>33.3</td>
<td>29.1</td>
</tr>
<tr>
<td>Boxelder</td>
<td>40.6</td>
<td>37.8</td>
<td>30.0</td>
</tr>
<tr>
<td>Maple, sugar</td>
<td>35.4</td>
<td>34.3</td>
<td>31.1</td>
</tr>
<tr>
<td>Alder, red</td>
<td>38.6</td>
<td>38.0</td>
<td>30.3</td>
</tr>
<tr>
<td>Birch, yellow</td>
<td>32.5</td>
<td>31.8</td>
<td>26.0</td>
</tr>
<tr>
<td>Birch, paper</td>
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<td>30.1</td>
<td>21.8</td>
</tr>
<tr>
<td>Pecan</td>
<td>33.5</td>
<td>30.7</td>
<td>23.3</td>
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<tr>
<td>Sweetgum</td>
<td>35.6</td>
<td>33.5</td>
<td>26.4</td>
</tr>
<tr>
<td>Blackgum</td>
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<td>27.2</td>
<td>22.4</td>
</tr>
<tr>
<td>Sycamore, American</td>
<td>40.9</td>
<td>39.0</td>
<td>31.1</td>
</tr>
<tr>
<td>Cottonwood, swamp</td>
<td>41.0</td>
<td>39.2</td>
<td>34.1</td>
</tr>
<tr>
<td>Aspen, quaking</td>
<td>41.4</td>
<td>39.7</td>
<td>34.9</td>
</tr>
<tr>
<td>Oak, white</td>
<td>27.8</td>
<td>28.2</td>
<td>21.2</td>
</tr>
<tr>
<td>Oak, northern red</td>
<td>32.4</td>
<td>31.7</td>
<td>28.3</td>
</tr>
<tr>
<td>Willow, black</td>
<td>42.9</td>
<td>43.4</td>
<td>35.4</td>
</tr>
<tr>
<td>Elm, American</td>
<td>37.0</td>
<td>35.4</td>
<td>27.0</td>
</tr>
</tbody>
</table>

\(^1\) Extractive-free bark extracted with 1 percent sodium hydroxide.

Figure 2.12: The variation in bark is clear from the highly detailed species level comparison of reducing sugar content. This exhaustive study was from a USDA report on bark.\[2\]
Figure 2.13: The variation in bark is clear from the highly detailed species level comparison reducing sugar composition. This exhaustive study was from a USDA report on bark.[2]

<table>
<thead>
<tr>
<th>Species</th>
<th>Glucose</th>
<th>Galactose</th>
<th>Manose</th>
<th>Arabinose</th>
<th>Xylose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fir, balsam</td>
<td>64</td>
<td>5</td>
<td>12</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>Larch, western</td>
<td>69</td>
<td>4</td>
<td>11</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>Spruce, Engelmann</td>
<td>61</td>
<td>5</td>
<td>9</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td>Spruce, black</td>
<td>64</td>
<td>6</td>
<td>7</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>Pine, jack</td>
<td>64</td>
<td>7</td>
<td>6</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>Pine, lodgepole</td>
<td>50</td>
<td>7</td>
<td>6</td>
<td>26</td>
<td>8</td>
</tr>
<tr>
<td>Pine, slash</td>
<td>63</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>15</td>
</tr>
<tr>
<td>Pine, sugar</td>
<td>69</td>
<td>6</td>
<td>8</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>Pine, western white</td>
<td>75</td>
<td>3</td>
<td>6</td>
<td>2</td>
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<tr>
<td>Hemlock, eastern</td>
<td>67</td>
<td>3</td>
<td>13</td>
<td>8</td>
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<tr>
<td>Boxelder</td>
<td>65</td>
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<td>2</td>
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<td>20</td>
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<td>Maple, sugar</td>
<td>63</td>
<td>3</td>
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<td>Alder, red</td>
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<td>6</td>
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<td>Birch, yellow</td>
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<td>1</td>
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<td>32</td>
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<tr>
<td>Birch, paper</td>
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\(^1\)Residue from the 1 percent sodium hydroxide extraction of extractive-free bark.
Lignin

Lignin’s main functions are as structural reinforcement in the cell wall, a barrier to microbial attack, and to minimize oxidative stress. This is achieved with its three dimensional cross-linked structure as shown in Figure 2.14. This amorphous polymer is made from three propenyl phenol monomers shown in Figure 2.15. Sinapyl alcohol (syringyl) and coniferyl alcohol (guaiacyl) are found in hardwoods, coniferyl alcohol in softwoods, and p-coumaryl alcohol and the aforementioned are all present in grasses. These monomers are polymerized via enzymes to produce C-C bonds and ether linkages at the α, β, and γ carbons or through an ether bond in between aromatic groups as shown in Figure 2.15c. From 2.15d it can be seen that a majority of the bonds are ether linkages linking the aromatic group of one unit to the aliphatic chain of another unit (α/β-O-4). The type of monomeric unit, linkages present, and the molecular weight of the lignin will affect how it cleaves and the extent. In Figure 2.16 it can be seen that a variety of degradation products are formed from the acid hydrolysis of lignin. Although not completely analogous to the acid glycolysis like in a liquefaction reaction, there are likely similarities. The details of how lignin behaves under the conditions of liquefaction will be discussed in later sections. Additionally, it should be noted here that lignin has a high degree of hydroxyl functionality as either primary, secondary, or phenolic alcohols. From Figure 2.17 it can be seen that slash pine and sugar pine have the highest lignin content of the barks studied at 50%, but lodgepole pine has the lowest of all barks studied at 15%. In Figure 2.5 it was shown that lodgepole pine had the highest amount of alkaline extracts. The low lignin content could be one reason for this high yield, since there is less of the lignin matrix to hinder hydrolysis. This stresses the fact that one must consider the species, since even within the genus of pinus the content of lignin can vary greatly.

![Figure 2.14: A model of the 3D-crosslinked amorphous structure of spruce lignin](image)
Figure 2.15: a) The three monomeric units of lignin, b) the types of linkages that join them[16] and c) their proportion.[16]
Figure 2.16: Lignin decomposition products from acid hydrolysis [18]
The variation in bark is clear from the highly detailed species level comparison of lignin content. This exhaustive study was from a USDA report on bark.\[2\]
2.1.3 Wood Structure and function

With the structures and some key aspects of lignocellulosics discussed, it only seems appropriate to now discuss how these intricate biopolymers have come together to form a remarkable composite, wood. The strength and ductility of wood is derived from the remarkable supramolecular arrangement of these three natural materials (cellulose, hemi-cellulose, and lignin) to form the tracheid cell. Longer tracheids are considered to be ideal fibers for improved mechanical properties and from Figure 2.18a a truly remarkable design can be seen. Starting from the middle lamellae, which is the interface between tracheid cells, it consists of pectin compounds that at maturity are lignified.[19] The primary wall is the first to be made followed by secondary walls (S1,S2,S3). The primary wall is elastic so microfibrils (discussed later - act as reinforcement and provide mechanical strength) are not orientated, but scattered in a matrix of hemi-cellulose and pectin compounds. The secondary walls which grow later have more cellulose and have helical arrays of microfibrils with orientation alternating between S1, S2, and S3. S1 tends to have a microfibril angle from 50-70° [20]. S2 which tends to be the thickest and therefore determines much of the mechanical properties, has a lower lignin content and microfibrils angles ranging from 5-30°. S3 has the lowest amount of lignin and a high microfibril angle of greater than 70°. It is the highly orientated microfibrils within each layer and the alternating orientation that provides strength. Some species like spruce do not have an S3 layer.[19]. Since the lumen, the middle of the tracheid, is for transport of water, it makes sense that S3 has the least amount of the highly hydrophobic lignin to facilitate transport.

On a smaller scale of an individual secondary cell wall, strength is afforded by the orientation and properties of the microfibrils. Microfibrils (up to 35 nm in diameter) are bound to one another by a lignin matrix. The microfibrils themselves are composed of elemental fibrils (3.5 nm) that are crystalline cellulose.[21] These elemental fibrils are within a matrix of amorphous cellulose and hemi-cellulose. The crystalline cellulose is due to linear chains of cellulose that align (via hydrogen bonding and the van der waals force) and it is this tight packing that makes cellulose resistant to degradation and hydrolysis.

This description shows that nature has reproduced a similar structure (fibers embedded with a matrix) at different length scales. This is part of the reason why wood is so resilient but had such a low density. In the previous sections the bark was looked at in terms of composition. However, this section makes it clear that although hemi-celluloses, extractives, amorphous cellulose can be more accessible because of their lack of crystallinity and improved solubility, some of these are still locked within hierarchical structures that can hinder accessibility. This becomes evident in the research chapters where pressure reactions are employed to achieve a greater yield.
Figure 2.18: a) An image showing the growth rings and a closer look at a tracheid cell of softwood (left) and hardwood (right) where L stands for the Lumen,[20] followed by b) a diagram illustrating a tracheid cell, a microfibril, and the elemental fibril.

2.1.4 Summary

By discussing the chemical components and structure of bark it becomes clear that bark contains many unique compounds, many of which possess features like aromaticity and a high hydroxyl functionality that would be useful as a raw material for the synthesis of polyols for making polyurethanes. However, liberating these compounds from the evolutionary designed structure meant to preserve them is no simple task. Although the above literature review showed various structures of sugars and extractives and lignin, these are not the structures that are found after their extraction. The various processes used to produce a polyol as discussed later (solvent treatment to produce an extract, liquefaction, alkoxylation) greatly alter the natural structures. Sometimes cleaving molecules to reduce molecular weight, sometimes derivitizing to increase molecular weight. Sometimes converting hydroxyl groups through oxidation into carbonyl or carboxyl groups, sometimes derivitizing them from phenolic to aliphatic hydroxyl groups. Herein lies the importance of polyol characterization, since the raw material changes from its natural structure to a liquefied polyol with structure and properties vastly different than before.

2.2 Key Polyol Characteristics

Before jumping into how biomass can be converted into a polyol, a brief discussion is needed on what the requirements are of a polyol. The key characteristics of a polyol are the functionality, the hydroxyl value / molecular weight / equivalent weight, the type of hydroxyl group, molecular structure, supramolecular structure, and colloidal stability / ageing. Some of these features are depicted in Figure 2.19.

- Functionality: Represents the number of reactive groups per molecule. When reacted with isocyanate this feature will dictate the network structure and cross-linking density, thereby influencing the glass transition temperature of the polymer and compressive behaviour.

- Hydroxyl Value / Molecular weight / Equivalent Weight: These are closely linked polyol char-
acteristics, but with different definitions. Hydroxyl value is a quantitative measure of hydroxyl groups as equivalents to KOH, and its standard unit is in mgKOH/g of sample. Molecular weight is simply the weight of the molecule. If functionality is fixed, then molecular weight is inversely proportional to hydroxyl value, i.e. the larger the molecule, the less hydroxyl groups per gram of sample. Equivalent weight ties together these two concepts, it represents the molecular weight per hydroxyl group. This definition is quite useful as it represents the chain length between cross-links.

- **Hydroxyl Type**: The four types of hydroxyl groups are phenolic, tertiary, secondary, and primary. The type of hydroxyl group is important for two reasons. Firstly, isocyanate reacts fastest with primary hydroxyls and water, followed by secondary hydroxyls. The use of catalysts can further intensify these differences in reaction rates.\[22, 23\] Secondly, the stability of a urethane linkage is related to the equilibrium between polymerization and depolymerization of a polyl and an isocyanate. Phenols react very slowly with isocyanate to produce unstable urethane linkages, while aliphatic alcohols react rapidly to yield thermally stable linkages.\[24\] It should be noted that the term polyl encompasses compounds with multiple hydroxyl or amine groups. However these are used primarily in spray polyurethane foams (PUFs), whereas this work is focused on polyols for rigid PUFs.

- **Molecular Structure**: Although a broad term, this refers more specifically to the presence of certain functional groups. For example, polyester based polyls hydrolyze more easily and are used for applications where biodegradation is desired, while polyether polyls are resistant to hydrolysis and exhibit slower biodegradation.\[25\]

- **Supramolecular structure**: This refers to the ability of the polyl to undergo intramolecular hydrogen bonding, going from an amorphous random coil to a structure with dense chain packing or even some crystallinity. This is especially relevant with large molecular weight polyls, whose supramolecular structure when characterized in the solution phase (highly accessible) could be very different than the properties it exhibits during a foaming polymerization reaction (compact and hidden reactive groups).

- **Colloidal Stability / Ageing**: The behaviour of the polyl over time is critical for practical application. One issue could be sedimentation. Large molecular weight polyls, especially that form supramolecular structures as described above, tend to precipitate as the polyl cools or progressively over time. This reduces the polyls homogeneity and introduces a shelf-time that would be unattractive for a commercial product like a polyl. Chromophores like aromatic rings or conjugated structures could also be lost over time due to exposure to UV or even visible light radiation. Therefore ageing may also manifest itself through a change in colour, or through degradation/polymerization of double bonds.

Since polyurethane foams themselves are very complex polymers, it is essential that the polyl component that they are made from is well characterized and consistent. This leads to more predictable foam behaviour and an understanding of the relationship between the structure of the polyl and the properties of the polyurethane foam.
Chapter 2. Literature Review

2.3 Methods for the Conversion of Biomass into a Polyol

The first step towards making a polyurethane polyol from bark is to extract the desired biopolymers from the biomass. There are multiple strategies to achieving this goal. The primary challenge has been to promote the depolymerization of the biopolymers and their functionalization and achieving a high extraction yield, while avoiding degradation (loss of hydroxyl groups). Early work performed solvent extractions on biomass to produce a solid extract, that was then mixed into liquid polyols to form a blend. The benefit of working with extracts is that through selection of an appropriate extraction process (temperature, time, solvent) the extract will have somewhat uniform behaviour. For example, an organosolv lignin extract will be more uniform in properties than ground bark that contains a broader range of biomolecules. Furthermore, these extracts could then be directly mixed into a polyol. Although facile, the extraction yield is often low and the extracts within the blend behaved more as a reactive filler. For these reasons, newer approaches have focused on the extraction of biomass via conversion into a liquid polyol, through depolymerization / functionalization of the biomass (the liquefaction approach) or the polymerization of the biomass (the alkoxylation approach). The research on extracts, liquefaction, and alkoxylation will be discussed in the following sections.

2.3.1 Extracts

With regard to extracts and their use in making polyols, most of the work has focused on tannins and lignins. The most common methods for the extraction of tannins are aqueous and aqueous solutions of acetone, methanol; commonly with a chemical additive to increase extraction yield or reduce viscosity like sodium hydroxide, [26, 27] sodium sulphite, [28] or to prevent phlobatannins/phylobaphenes formation with addition of either urea, phloroglucinol or m-phenylenediamine [29].

The use of sodium hydroxide is by far the most commonly used and most reported. Alkaline treat-
ments have been shown to solubilize phenolic compounds, swell the biopolymer matrix, and reduce crystallinity.\cite{30} In a study by Vazquez \cite{31} it was found that increasing the NaOH concentration from 2.5 \% to 5 \% increased the yield from 23 \% to 25 \%, but with the repercussion that the stiasny number decreased from 96 \% to 81 \%.\cite{31} The stiasny number reflects the reactivity of phenolic rings to formaldehyde, and thus one can infer some sort of degradation occurred with greater concentration of NaOH despite the higher yield; and therefore the amount of NaOH should be limited to below 2.5 \%. This should also highlight the fact that extraction yield is often maximized with little regard for the extent of degradation, since the extent of degradation is more difficult to assess.

The use of sulfites has also been reported to increase yield and reduce viscosity. It has been shown to increase yield through cleavage of the interflavanoid tannin linkages, thus making the polymers into oligomers, consequently liberating them and increasing their solubility.\cite{28} This is achieved through a ring opening of the C ring, addition of a hydroxyl group, and addition of a sulphon group at position 3 (Figure 2.7). The addition of the highly polar group increases the solubility of the compound.\cite{29}

During extraction effort has been made to minimize the reorganization, recondensation, and polymerization of the tannins. The reorganization of tannin forms highly insoluble compounds known as phlobatannin or phlobaphenes as shown in Figure 2.20a. It was found that when performing aqueous extractions the amount of tannin converted to phlobatannin was 6 \% of the total tannin content, when sulphite was added to increase the yield it was found that up to 40 \% of the tannin extracted was converted into phlobatannin.\cite{29} The self-condensation can be attributed to either of the mechanisms shown in Figure 2.20b and c that depict the formation of the reactive carbocation through ring-opening or cleavage of the interflavanoid bond. These effects can be lessened through the addition of a nucleophillic agent like urea that has a greater reactivity than that of the activated tannin species. Essentially, the reactive carbocation on the tannin reacts with urea before it can find another tannin molecule to form the phlobatannin.\cite{29} It is also believed that urea alters the aggregation properties by helping solvate the previously insoluble molecules.\cite{32}

These results exemplify the difficulty of biomass conversion. Even when mild aqueous extractions are done, significant degradation / chemical modification can occur. Attempts to mitigate this damage often result in a lowering of the conversion yield.

Another extract that is commonly used is lignin. The extraction of lignin has plagued pulp and paper industries for many years, the nefarious cross-linker is able to bind cellulose, and together with hemi-cellulose pose considerable challenges to converting these materials into usable high value materials. Thus the first step to the utilization of lignocellulosic biomass is extracting lignin, the gate-keeper to cellulose. The phrase high value material is also key, traditionally the pulping processes are able to produce a large amount of lignin as a side product, but only after harsh chemical treatments have degraded it substantially. The fragmentation of this macromolecule occurs via cleavage of the ether linkages; however, the reactive species formed can then undergo condensation reactions that form C-C bonds. These are stronger than the initial ether bonds and may increase the molecular weight of the lignin.\cite{33}

Lignin has a molecular weight ranging from $10^3 - 10^5$, and for organosolv lignin it ranges from $2.7x10^3 - 1.1x10^4$\cite{18}. Organosolv treatments employ various low boiling solvents that extract and depolymerize the lignin, and seems to have lots of potential in reducing the molecular weight. A study that varied the amount of ethanol, temperature, and acid content, produced lignin with a molecular weight ranging from 1000 - 4000 Da.\cite{34} Another strategy to breakdown lignin into smaller fragments
Figure 2.20: a) formation and structure of phlobatannin, creation of reactive tannin through b) ring opening or c) cleavage of interflavanoid linkage, and d) the reaction with urea to prevent self-condensation.
is through hydrolysis. Hydrolysis with acetic acid could reduce the molecular weight to within 2000-
4000 Da.[35]. More interestingly, hydrolysis with sodium hydroxide and various aromatic phenols was
found to greatly improve the solubility and prevent recondensation of lignin. With the addition of 1.4
moles of resorcinol / per phenyl propane unit of lignin the hydrolyzed product was completely soluble in
dioxane.[36] Aside from typical organic solvents, there is much excitement in the new field of ionic liquids
as these green solvents show great promise for the dissolution of various forms of biomass. Their green
tag stems from their ability to be recycled and low volatility of organic compounds. It was found that
the ionic liquid 1-ethyl-3-methylimidazoliumacetate has a high lignin solubility (300g/kg) and a poor
wood flour solubility (30g/kg).[37] This selectivity allows lignin to be dissolved in the ionic liquid (an
subsequently precipitated for collection), while the cellulose residue is now in a highly accessible state
after delignification. As this process does not rely on bond cleavage it keeps the lignin in a natural state,
and is able to achieve a lignin yield of 63 % of the total lignin amount under mild conditions.[37, 38] The
lignin extracts produced via hydrolysis, organosolv treatments, or with ionic liquids have shown some
promise in being used as polyols and made into PUFs. This will be discussed in a later section that
reviews PUFs made from the thermo-mechanical blending of biomass into polyols to make biomass-based
foams.

2.3.2 Liquefaction

Liquefaction uses harsh conditions and a solvent to fragment biomass through hydrolysis / phenolysis /
alcoholysis reactions that cause the biopolymers to undergo dehydration, dehydrogenation, deoxygenna-
tion and decarboxylation. At the same time, competing side reactions of condensation, cyclization, and
polymerization can increase molecular weight.[39] The word harsh is also quite relative, as thermal liq-
uefaction through pyrolysis can be done at temperatures of 600 - 1200 K, [40]. Pyrolysis and gasification
techniques are also targeted towards small molecular weight products or even gasses, and therefore the
amount of degradation or depolymerization is far greater. Consequently demanding a greater energy
footprint.[40] In contrast, solvolytic liquefaction can be done at temperatures ranging from 400 - 600 K
and pressurized up to 20 MPa. The primary advantage of the solvolytic approach is that the solvent
dilutes the reactants, helping reduce cross-linking and recondensation side reactions.

With regard to solvolytic liquefaction of biomass, two of the most common solvents are phenol and
polyhydric alcohols. In the phenol-formaldehyde (PF) resin industry it is common to use phenol to
liquify the biomass. This has been done for lignin,[41] corn bran,[42] wood, [43] and bark. [44, 45, 46]
As phenol is of course used in the creation of a PF resin its remnants are not of importance; however
in a polyurethane, excess phenol will be deleterious to the properties as it will simply terminate the
polymerization. For this reason the use of polyhydric alcohols (multiple alcohol groups) has become
quite popular as a solvent since they can be readily included in a polyurethane formulation.

**Liquefaction Conditions** Typical polyhydric solvolysis reactions utilize combinations of polyethylene
glycol (PEG), polypropylene glycol (PPG), glycerol, and sometimes low-boiling alcohols (methanol and
ethanol); a temperature range from 150 - 250 °C; reaction duration of thirty minutes to three hours;
and finally phosphoric acid, organic acids, and sulfuric acid as catalysts. These were performed on a
variety of biomass types such as wood [47, 48, 49, 50, 51, 52] starch,[53] paper,[53], and bark.[54, 55, 56]
Depending on a plethora of variables (of which the most important being time, temperature, catalyst
content, and solvent-biomass ratio) the biomass can be completely liquefied and ready to use to make a
polyurethane with little purification.

The liquefaction of wood has been described as a three stage process: \[52\] first rapid as lignin, hemicelluloses, and amorphous cellulose are attacked, the second is gradual as crystalline cellulose is penetrated by acid; the third constitutes a reversal of the yield as recondensation reactions can occur, shown to be promoted by the presence of lignin, \[57\] and presumably phenolic extractives would behave similarly. These stages can be seen in Figure 2.21a, with the recondensation reactions most prevalent at high temperature. Much of the literature work has focused on achieving a high conversion yield, while the characterization of the polyol was neglected to an extent. For example, high temperatures were often used that caused significant degradation. In Figure 2.21 a) the effect of temperature can be seen on the conversion yield; however, greater analysis into how temperature affects degradation is lacking and needs to be addressed.

Regarding the other reaction conditions, the literature has shown that a high solvent to biomass ratio and a glycerol content from 10 - 30 wt. % (as shown in Figure 2.21 b) and c) are conducive to achieving a good yield and preventing recondensation reactions of phenolics. \[58, 57\] The reason is that the high amount of solvent makes phenolic compounds more likely to condense with the solvent instead of reacting with other phenolic groups, hindering insoluble precipitate formation. Glycerol is highly effective due to its low molecular weight enabling a high molar concentration of hydroxyl groups. Finally, the type and amount of catalyst has a strong impact on the yield. This is said to be mainly dependent on the hydronium concentration produced, therefore inorganic acids produce a greater proton concentration/per mole of acid added versus their larger molecular weight organic acid counterparts. \[59\]

It is important to note that this polyol material is a slurry of biomass degradation products, chemically modified biomass, solubilized biomass, and the polyhydric solvent used to liquefy. Therefore to study and understand the properties of a PUF, it is essential that the structure of the polyol is characterized thoroughly. The polyhydric alcohol solvent has often been attributed with preventing recondensation reactions (i.e. the use of glycerol). However, understanding how variation in the polyhydric alcohol structure can influence degradation has not been discussed in greater depth.

**Liquefaction behaviour of biopolymers** Prior work done on bark-based PUFs through liquefaction focused mostly on the foam properties with limited attempts to systematically investigate the impact of the liquefaction conditions on properties of the bark-based polyols. \[60, 54\] In some studies, bark was liquefied at high temperatures using the bisulfite method to produce polyurethane foams and films. \[61, 62\] At 250 °C these polyols were shown to contain tannin degradation products featuring phenolic compounds with varying degree of acetyl, methyl, and hydroxyl functionalities. \[63\]

The behaviour of cellulose and lignin under liquefaction has been explored quite thoroughly. Yamada et al. \[64, 65\] and Jasiukaityte et al. \[59\] studied the liquefaction of cellulose and wood and found that liquefaction at higher temperatures, like 150 °C, was too harsh and resulted in substantial degradation of cellulose to levulinate esters (Figure 2.22a). At this temperature, lignin was modified by glycols undergoing condensation reactions with the phenolic hydroxyl groups to produce aliphatic hydroxyl groups (Figure 2.22b). \[66\] In the case of cellulose, a molecule with lots of hydroxyl functionality is degraded into a compound with only one reactive group. In the case of lignin, the lignin hydroxyl groups are made more accessible. Therefore, liquefaction has a clear benefit for types of biomass that are rich in phenolic compounds!

However, their studies did not look into the liquefaction behaviour of wood and cellulose at lower
Figure 2.21: Effect of a) temperature, b) solvent to biomass ratio, and c) glycerol content on liquefaction yield [58]

Figure 2.22: The reactions involved in the a) degradation of sugar and the b) derivitization of lignin
temperatures. Nor has there been a similar study investigating the liquefaction behaviour of extractive type compounds that would be found in bark. One study that is relevant is by Kurth et al., where condensed tannins from softwood bark underwent alcoholysis with ethanol. Under the mild conditions of ethanol reflux, tannins would breakdown into simpler phenolics like catechol and phloroglucinol. Therefore, similar products would likely be formed when liquefied in the presence of polyhydric alcohols like glycols. However, since liquefaction is also under acidic conditions, this will cause the phenolics to undergo condensation, as was shown by researchers working with lignin. These results give us some insight into the behaviour of cellulose, lignin, and tannins when liquefied. However, understanding how temperature impacts composition and degradation, how solvent structure can be used to improve selectivity, or in-depth characterization of the molecular weight and alcohol type are insights that are lacking from the literature, but will be addressed in this work. Since properties of the polyurethane foams depend on the molecular structure and properties of the polyols, it is crucial to determine how the liquefaction conditions affect key characteristics of the bark polyols.

2.3.3 Alkoxylation

Industrial polyether polyols are produced using the alkoxylation process, whereby hydroxyl containing compounds like glycerol, sugars, and glycols are used as seed compounds and are polymerized upon through a reaction with propylene oxide (PO) to produce chain extended polyols with tunable properties. This is a well established process for petroleum-based polyols and it would be highly beneficial to explore whether the same process is well suited for the conversion of unique compounds found in a biomass material like bark.

Alkoxylation, or more specifically propoxylation, chain extends molecules with hydroxyl functionality through a base-catalyzed anionic ring-opening polymerization of PO. This is an appealing process since it can be done under alkaline conditions that will result in less degradation of sugars compared to the strongly acidic and oxidizing conditions in a liquefaction; the high pressure and temperature produce high yields; and most importantly, the alkoxylation of sugar, glycerol, and short glycols is already a common practice in industry to produce polyols. Alkoxylation has already been performed on a variety of biomass resources such as cork, starch, sugar beet, date seeds, chitin/chitosan, lignin, and tannin. Before the alkoxylation of biomass is discussed in detail, it might prove more useful to discuss the different reactions occurring and how industry has been using alkoxylation to produce its polyols from seed compounds like sugar and glycerol.

The process of alkoxylation entails four reactions shown in Figure 2.23. Initially, KOH reacts with the seed compound to produce an alcoholate and releases water, as shown in reaction 1. The alcoholate reacts with PO to produce the copolymer phase (seed compounds with grafted polypropylene glycol chains) as shown in reaction 2a and 3. Water released from the reaction with KOH and bound water present in the biomass reacts with PO to produce the homopolymer phase (polypropylene glycol diols) as shown in reaction 4. Although the alcoholate primarily reacts with PO to form a growing polymer chain, under certain conditions PO acts as a ligand for the alcoholate and abstracts a proton from the methyl of PO. A chain transfer reaction to the monomer occurs, resulting in a rearrangement that yields an allyl alcohol, or a further rearrange to produce propenyl alcohol as shown in reaction 2b. This unwanted side reaction reduces polyol functionality since an unsaturated end-group is formed instead of a hydroxyl end-group. As shown in reaction 2a, this rarely happens in polymerizations where a low amount of PO is used relative to the seed compound. This is because hydroxyl groups act as a better ligand than PO.
for the alcoloholate.\cite{68} Therefore, the high concentration of hydroxyls in seed compounds and their lone pairs complexing with potassium reduce the prevalence of the chain transfer reaction.

Figure 2.23: Various hydroxyl containing compounds (R= sugars, tannins, terpenoids, and lignins) found in bark that 1) react with KOH to form an alcoloholate and water. 2a and 3) PO reacts with the alcoloholate to form polypropylene glycol chains grafted onto the bark compounds and 4) PO reacts with water to form polypropylene glycol diols. 2b) A chain transfer side-reaction can occur where the growing chain is terminated through abstraction of a proton from the monomer. The monomer then rearranges and has an unsaturated end-group. This reaction can be minimized through the use of ligands (L).

The reaction described above is typical of PO polymerization onto some type of biomass compound with reactive hydroxyl groups acting as seed compounds. However, alkoxylation in industry is often performed using ethylene oxide (EO), PO, or combinations of the two to make block copolymers; with various seed compounds as shown in Figure 2.24; and using either KOH as a catalyst or a double metal cyanide catalyst (DMC). From looking at this list of seed compounds it can be seen how easy it is to control the functionality through simple selection of an appropriate seed compound. The molecular weight is mostly controlled by the amount of monomer added since the reaction almost behaves like a living polymerization (new chains do not initiate). The reason it is not considered a fully living polymerization is because of reaction 2b shown in Figure 2.23. The formation of unsaturation creates a new chain. However, this side reaction only becomes prevalent when very large molecular weight polyols are pursued (a high PO to seed ratio), and to a lesser extent is dependent on temperature, and catalyst type. For example, long chain glycols like PPG-2000 can have up to 4-20 olefinic terminal end-groups per 100 molecules.\cite{79}

The selection of an appropriate catalyst is quite crucial. Potassium hydroxide is inexpensive and
commonly used. However, for large molecular weight polymers KOH will promote the unsaturation reaction. Under these conditions, a DMC catalyst is used instead. DMC catalysts are a family of complexes based upon nonstoichiometric complexes of $\text{Zn}_3[\text{Co(CN)}_6]_3 \ast \text{ZnCl}_2$. They can be up to 1000 times more active than KOH at polymerizing PO; however, they cannot be used at all for the polymerization of EO, and they are more expensive. Therefore, the appropriate selection of the catalyst is crucial to design of the polyol if larger molecular weight polyols are targeted, i.e. for flexible PUFs.

### 2.3.4 Conversion of Plant Oils into Polyols

Creating a polyol from lignocellulosic materials entails a different set of challenges than that of a polyol derived from plant oils. Although there are some serious socio-economic reasons for curtailing the use of plant oils, their molecular structures and the developments in the chemistry of their modification are very promising. It can be seen from Figure 2.25 the general structure of a plant oil, a triglyceride with fatty chains. The double bonds in these fatty chains can be chemically modified into hydroxyl groups. When this is done, you are left with a trifunctional-glycerol based polyol. This is in fact very similar to what industry uses currently in many foam formulations. However, there are also some highly critical technical issues that still need to be addressed with their use.

One critical issue is the low glass transition temperature of the polyurethanes made from these polyols. In palm kernal oil, nearly half of the fatty chains have no double bond, which means the functionality of the polyol will be considerably lower. Soy plant oil has 15% of its chains saturated which not only adds zero functionality, but also contributes a dangling chain to the polyurethane foam network that plastisizes the polymer network and prevents crystallinity. This is manifested as a low glass transition temperature and low rigidity. The length of these fatty chains is also quite important, because if the double bond is located in the middle of an eighteen carbon length chain, when incorporated into a polymer network, once again there is a long dangling chain that reduces rigidity. This is clear from the low glass transition values of PUFs made from plant oil polyols: canola (32 °C), soybean (31 °C), linseed

<table>
<thead>
<tr>
<th>Starter</th>
<th>f</th>
<th>Structure</th>
<th>Molecular weight (daltons)</th>
<th>Hydroxyl number (mg KOH/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>2</td>
<td>HOH</td>
<td>18</td>
<td>6233.3</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>2</td>
<td>HOCH$_2$CH$_2$OH</td>
<td>62</td>
<td>1807.9</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>2</td>
<td>HOCH$_2$CH$_2$OCH$_2$OH</td>
<td>106</td>
<td>1057.4</td>
</tr>
<tr>
<td>1,2 Propylene glycol</td>
<td>2</td>
<td>CH$_3$HOCH$_2$CHOH</td>
<td>76.1</td>
<td>1474.6</td>
</tr>
<tr>
<td>Dipropylene glycol</td>
<td>2</td>
<td>CH$_3$HOCH$_2$CHOH</td>
<td>134.2</td>
<td>836.3</td>
</tr>
<tr>
<td>Glycerine</td>
<td>3</td>
<td>OH</td>
<td>92</td>
<td>1829</td>
</tr>
<tr>
<td>Trimethylol propane</td>
<td>3</td>
<td>CH$_3$CH$_2$OH$_2$OH</td>
<td>134.2</td>
<td>1254.1</td>
</tr>
<tr>
<td>1,2,6 Hexanetriol</td>
<td>3</td>
<td>OH</td>
<td>134</td>
<td>1255</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>3</td>
<td>N(CH$_2$CH$_2$OH)$_3$</td>
<td>146</td>
<td>1152.7</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>4</td>
<td>H$_2$NCH$_2$CH$_2$NH$_2$</td>
<td>60</td>
<td>3740</td>
</tr>
<tr>
<td>Pentaoxyrthitol</td>
<td>4</td>
<td>C$_5$H$_7$OH$_4$</td>
<td>136.15</td>
<td>1648.18</td>
</tr>
</tbody>
</table>
(77 °C), sunflower (32 °C), corn (30 °C).[81] Low glass transition temperature polyurethanes are ideal for cushioning and more flexible foams. In fact, Recticel is Europe’s largest flexible foam manufacturer and have incorporated a soybean oil polyol into their foams.[81] However, they are not suitable for rigid foam applications.

Another impediment to the use of plant oil based-polyols is the complexity and cost of their modification. In Figure 2.26 some of the most common reactions are depicted. One of the earliest approaches is a transesterification reaction (1) where the triglyceride is reacted with an alcohol, that yields glycerol and the previous alcohol is grafted with an alkyl ester chain. These products are not ideal for a polyol, but have found great utility in the manufacturing of biodiesel. The next two reactions are based on conversion of the double bond into a hydroxyl group, the first through epoxidation (2) and the latter through oxidation (3). In epoxidation, hydrogen peroxide is used to convert the double bond into an oxirane, whose ring is then opened in the presence of methanol to produce hydroxyl groups. In the oxidation method, oxygen and light are used to oxidize the double bond into a carboxylic acid, that is then reduced to a hydroxyl group. Both of these polyols suffer from having hydroxyl groups within the middle of the aliphatic chain, which results in the low rigidity issue as described above. Two approaches to counter this are based upon a polymerization of the fatty acid chain (4) or a cleavage of the chain at the double bond (5). The polymerization requires a fatty chain used as the monomer and through a cyclotrimerization of the double bond yields an aromatic polyol, whose acid end-groups can be converted into hydroxyl groups. In the chain cleavage Ozonolysis reaction, ozone is used to fragment the triglyceride at the double bond and then react it with a simple diol. The cleaved portion can be removed through purification, while the triglyceride now has a functionality of three hydroxyl groups, all as the pendant groups, rather than in the middle of the chain.

This discussion was not meant to be exhaustive, nor explain the chemistry in full detail, but rather to show the diverse approaches and progress made in the development of polyols from plant oils. It is clear that polyols with high functionality can be made from plant oils, but the suitability for rigid foam applications and the economics/complexity of their modification are issues that are still being investigated.

![Figure 2.25: The variation in chain length and double bond frequency among various plant oils](image-url)
Figure 2.26: Various reactions used to convert triglycerides and acids from plant oils into polyols [80]
2.3.5 Summary

The research described showed that polyols derived from natural resources are a viable solution. From simple methods involving dissolution, the approaches for lignocellulosic biomass conversion have evolved into two approaches: that of depolymerization via liquefaction and of grafting via alkoxylation. Whereas, the usage of plant oils faces its own unique challenges for gaining entry into commercial use. The polyols synthesized by these methods were used to make PUFs and their characteristics are discussed in the following section. The complexities of a polyol made from biomass can be a hindrance to their characterization. In some cases making a PUF is a more practical way to assess the utility of these polyols, and to make inferences about their structure by the properties the foams exhibit.

2.4 Polyurethane Foams

2.4.1 Components and Formulation

Without delving too deeply into polyurethane foam formulations as it is quite the expansive topic, it should suffice to make brief comments on the use and terminology regarding catalysts, surfactants, blowing agents, and the isocyanate; in order to facilitate an understanding of how these will dictate material properties and be impacted through the use of bark-based polyols.

- Catalysts: The catalysts in polyurethanes are often grouped into categories based on their different function. For the purposes of this review, only blow and gel were investigated, of which organo-tin and tertiary amine catalysts are the most commonly used. The distinction between the two types is defined by their affinity (i.e. ability to hydrogen bond) with water (blow) or the polyol (gel). Therefore, catalysts react with both, but tend to excel at one better than the other. Figure 2.27 shows the structure of triethylenediamine (TEDA) and a triamine compound that both have good gelling activity as represented by their blow / gel ratio of 0.2 and 0.3 respectively.[82] Whereas the ether has better blowing activity at a ratio of 2.4. It is believed that ether groups stabilize the water molecule in order to facilitate chelation via methyl groups.[82] The relevance of this to this project is that polyols derived from bark could have a variety of hydroxyl groups, and may not be catalyzed as expected.

- Surfactants: A surfactant has important roles in the following foaming processes: dispersion of reactants, nucleation, stabilization, and cell opening in flexible PU foams.[83] In all cases, it acts to reduce the surface energy of the interface between the blowing agent (in liquid or gaseous form) with the polymer (liquid or solid). The polymerization of a liquid monomer into a solid polymer, in conjunction with a dispersed liquid phase that boils or reacts to form an encapsulated gas is a complex process. In order to ensure that these different states of matter are stabilized a surfactant is used, and if successful results in a controlled and uniform morphology (cell size, size homogeneity, closed-cell content).

- Blowing Agents: Water is primarily used due to its innocuous nature as it reacts to produce CO$_2$, which expands the polymer into a foam. However since water reacts with isocyanate this increases the amount of isocyanate required, incurring greater cost through use of an expensive chemical derived from petroleum. The amount of water will dictate the density, the reaction rate due to its highly exothermic reaction, and also the microphase-separation (water forms the urea hard
segment). Hard segment refers to the urea rich regions of the polymer, that impart stiffness and rigidity. Excessive hard segment fraction leads to brittle and friable foams (a material that easily crumbles). Furthermore, the small size of carbon dioxide allows it to diffuse out of the polymer over time, resulting in deformation over time.[84]

If water is not used, then physical blowing agents (liquids with low boiling points) or chemical blowing agents (chemicals that react to release a gas) are used. Many physical blowing agents used in the past belonged to families of compounds like chlorofluoro hydrocarbons (CFCs - carbon is fully substituted with halogens) or halogenated chlorofluoro hydrocarbons (HCFC - carbons are partially substituted with halogens) as shown in Figure 2.27. The prior have been nearly phased out due to their damaging effect on the ozone layer of the earth, the latter are being used as an intermediate solution since these compounds are less damaging to the ozone, but are very potent greenhouse warming gasses. The advantages of these compounds are their low boiling point, low heat of vaporization, low thermal conductivity, they are non-flammable, and non-toxic.[84] One alternative is to use simple hydrocarbons like pentane; however, their flammability is a safety concern.

- Isocyanate: The structures of the most commonly used isocyanates (polymeric MDI, MDI, HMDI, and TDI) are shown in Figure 2.27. The reactive isocyante group, NCO, will react in a multitude of ways: with itself forming dimers (uretidinedione) and trimers (isocyanurate); with active hydrogen compounds, alcohols react to form urethanes and amines to form ureas; and even undergo secondary reactions when reacted with a urethane to form an allophanate, and with a urea to form a biuret. These reactions are shown in Figure 2.28. Although complex, for the purposes of a simple formulation for a rigid PUF, the reaction with an alcohol to yield the urethane linkage and the reaction with water to yield a urea linkage are most relevant. Key isocyanate features are the functionality (the number of isocyanate groups per molecule), the equivalent weight (the number of reactive groups divided by the molecular weight), the molecular backbone structure (polymeric, aromatic vs. aliphatic, substitutions), and viscosity. It can be seen that many of these mirror the key characteristics of a polyol. In this work however, a very standard isocyanate was used, polymeric MDI, (commercial name is Rubinate M), with an average functionality of 2.7. A functionality value of greater than 2 enables PUFs to be a thermo-set networked polymer with a high degree of cross-linking. This is further controlled through the isocyanate index.

Isocyanate index (ICI) is the ratio of NCO groups to OH groups, shown in Equation 2.1. Where ICI is the isocyanate index (an isocyanate index of 1.1 translates into a 10 % excess of isocyanate groups), \( M_{IC} \) is the mmol of NCO groups per gram of sample, \( W_{IC} \) is grams of isocyanate, \( M_p \) is the hydroxyl value of the polyol in mmol/g, \( W_p \) is the weight of polyol, \( M_{H2O} \) is the mmol/g of OH groups and \( W_{H2O} \) is grams of water. This ratio is quite crucial as it will impact many of the polymer characteristics from the cross-linking density, glass transition temperature, and youngs modulus, which will dictate the brittle or flexible nature of the foam. Many flexible foams are made with an ICI of <1, while rigid foams have an ICI of >1. When an ICI is much greater than 1, the formation of isocyanate dimers, trimers, and secondary reactions become more pronounced. As these components are introduced the polymeric structure becomes more thermoset in nature and extremely rigid and brittle.
Chapter 2. Literature Review

\[ ICI = \frac{M_{IC} W_{IC}}{M_{WP} W_{WP} + M_{H2O} W_{H2O}} \]  

(2.1)

Figure 2.27: Typical catalysts, isocyanates, and the general structure of a silicone surfactants and blowing agents used in formulations of PUFs

The purpose of discussing these different components is to stress the fact that formulation plays a key role in determining foam properties. Therefore, when surveying published results in the next section, it is rather difficult to make comparisons since researchers often vary important parameters like the isocyanate index and the type of isocyanate. A change in the catalyst content from 1 % to 2 % by weight relative to the polyol, seems like a small change, but could drastically effect the foam morphology and foam properties. Many aspects of the polymer structure and the morphology can all be impacted through formulation changes. This makes understanding the effect of adding a biomass component difficult to assess, which is why control samples are often implemented to facilitate a better comparison.
Figure 2.28: The common reactions and side reactions of isocyanate. Image was taken from Chattopadhyay et al. [24].
2.4.2 Survey of Biomass-Based PUs

In the field of rigid polyurethane foams, two of the main design criteria are the compressive behaviour and the insulative properties. Both of these are complex to discuss since there are a multitude of polymer and foam characteristics that they are dependent upon. The focus of this review is on the compressive behaviour, so some of the pertinent fundamental polymer and foam properties of biomass-based PUFs will be discussed, including the cross-linking density, glass transition temperature, the polymer structure (functional groups, crystallinity) and morphology.

Crosslinking-Density

The formation of cross-links in a polymer is essential to forming a thermoset polymer, i.e. a polymer with a connected network of polymer chains. This increases rigidity, but also impacts thermal stability and fatigue behaviour. As the cross-linking density increases, a material will transition from being highly resilient like rubber to something very brittle like an epoxy. The crosslinking density can be increased in two ways, by increasing the functionality of the monomers (polyol or the isocyanate) so that connectivity increases or by decreasing the molecular weight of the monomers so that the distance between chains decreases. Even in a well defined PU polymer where the functionalities and molecular weights of both monomers are known, the actual determination of the value however is quite difficult. Therefore approximations are based upon more measurable features like stress and strain data or by solvent swelling as shown by Equation 2.2.\[85\] Where $\nu_c = \text{moles of cross-links}$; $V_o = \text{dry volume}$; $V_\infty = \text{swollen volume}$; $\chi = \text{polymer-solvent interaction parameter}$; $\nu = \frac{V_o}{V_\infty}$; $V_1 = \text{molar volume of the solvent}$.

$$\frac{\nu_c}{V_o} = \frac{-2(\nu + \chi \nu^2 + \ln(1 - \nu))}{V_1(2\nu^4) - \nu} \quad (2.2)$$

A biomass polyol will consist of polymers with various chain lengths and functionalities producing a variety of cross-linking configurations as shown in Figure 2.29. Ideally, the cross-links would join one polyol component to another (B); however, this is not the case when bonds are left dangling (A, C), nor are all cross-links effective at building a network (D,E). Some of these have been described in the literature below.

Biopolymers have very high levels of functionality, e.g. a single molecule of glucose has five reactive OH groups, but it is sterically unlikely that all would react to form urethane linkages. This was demonstrated in experiments where the degree of conversion of isocyanate groups was measured via FTIR after reacting for thirty minutes.[86] It is evident from Figure 2.30 that increasing the amount of lignin component in the polyester-based polyol will decrease the conversion. One explanation is that the sterically hindered alcohols of the lignin could not react with the isocyanate. The more dominant effect was that long polyester polyol chains, molar mass between 400-1000 Da, would dilute the isocyanate, a reactive group adrift in a sea of hydrocarbons indifferent to it, and consequently reduce the conversion of NCO groups. This may have also happened with the lignin, since lignin’s molecular weight can be quite large. This indicates that isocyanate may become trapped in large molecular weight biopolymers. It was expected that the high functionality would lead to a highly cross-linked polymer; however, the low conversion of isocyanate would result in a less cohesive network. This stresses the fact that a high functionality polyol must also be accessible. In work done on lignin based PUFs,[87] it was found that the cross-linking density was greatly impacted by the polyhydric solvent chain length, rather than lignin content. They believed that only long chains once tethered could migrate within the polymer to form
Figure 2.29: Diagram illustrating how polyols that are a) short, cannot reach to form cross-links; b) of medium length, form good cross-links; c) too long, dilute the reactive OH or NCO group; d) polyfunctional, may form internal cross-links; e) short, may cross-link with same molecule

A cross-link. This result is shown in Figure 2.31a. A different study on liquefied wood based-PUFs with a very low biomass fraction showed a slight improvement in cross-linking density with increased biomass(Figure 2.31b), but showed quite dramatically how increasing the isocyanate index is the main factor dictating the cross-linking density (Figure 2.31c).

<table>
<thead>
<tr>
<th>Sample</th>
<th>PCL</th>
<th>Lignin content (wt.%)</th>
<th>Isocyanate conversion (30 min)</th>
<th>Coefficient of variation* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(400-10)</td>
<td>400</td>
<td>10</td>
<td>0.9837</td>
<td>0.36</td>
</tr>
<tr>
<td>A(400-15)</td>
<td>400</td>
<td>15</td>
<td>0.9841</td>
<td>0.17</td>
</tr>
<tr>
<td>A(400-20)</td>
<td>400</td>
<td>20</td>
<td>0.9799</td>
<td>0.55</td>
</tr>
<tr>
<td>A(400-25)</td>
<td>400</td>
<td>25</td>
<td>0.9798</td>
<td>0.58</td>
</tr>
<tr>
<td>A(750-10)</td>
<td>750</td>
<td>10</td>
<td>0.9031</td>
<td>1.20</td>
</tr>
<tr>
<td>A(750-15)</td>
<td>750</td>
<td>15</td>
<td>0.9029</td>
<td>1.10</td>
</tr>
<tr>
<td>A(750-20)</td>
<td>750</td>
<td>20</td>
<td>0.8606</td>
<td>1.30</td>
</tr>
<tr>
<td>A(750-25)</td>
<td>750</td>
<td>25</td>
<td>0.8453</td>
<td>0.25</td>
</tr>
<tr>
<td>A(1000-10)</td>
<td>1000</td>
<td>10</td>
<td>0.8254</td>
<td>1.40</td>
</tr>
<tr>
<td>A(1000-15)</td>
<td>1000</td>
<td>15</td>
<td>0.8059</td>
<td>0.42</td>
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<tr>
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<td>0.37</td>
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<tr>
<td>A(1000-25)</td>
<td>1000</td>
<td>25</td>
<td>0.7173</td>
<td>0.04</td>
</tr>
</tbody>
</table>

* Coefficient of variation: CV = s/x × 100.

Figure 2.30: Effect of Lignin amount and PCl (polycaprolactone) chain length on NCO conversion [86]

These studies were done on films. Foams are not conducive to determining the cross-linking density since they act as sponges retaining solvent, and become too difficult to measure expansion accurately. A different approach is to examine the soluble fraction;[88] i.e. the chains that are not cross-linked and leached out through a solvent treatment. This approach seems to be better suited to foams as it relies upon a change in mass due to leaching, versus measurements of volume expansion in the previous method. The equations for this are shown in Equations 2.3, 2.4, 2.5 where W=soluble fraction; \( w_1 = \) dry weight before extraction; \( w_2 = \) dry weight after extraction; \( \theta_2 = \) polymer volume fraction; \( \rho_2 = \) density of the PU, \( \rho = \) density of the solvent.

\[
W_s = \frac{w_1 - w_2}{w_1} \tag{2.3}
\]
Figure 2.31: a) Cross-linking density as a function of lignin content and the chain length of PEG [87]; Dependence of cross-linking density on b) the biomass content (Wood-PUF, ICI=1) as well as c) ICI [85].
Glass Transition Temperature

The glass transition temperature, $T_g$, is the temperature below which polymer chains do not have sufficient energy to undergo reptation, snake-like thermal motion, and thus behave glassy or brittle. Biomass PUFs tend to have a high $T_g$. Firstly, biomass contains high functionality polyols and cross-linking restricts chain motion.[58] Secondly, aromatic groups as well as double bonds in the phenylpropene unit of lignin prevent rotation and induce rigidity.[87] When comparing a liquefied wood PU film to a control, even when cross-linking density and ICI were similar, the biomass PU film showed a higher tensile strength due to the steric induced rigidity and stiffness.[85] By understanding how different components impact the $T_g$ it is possible to customize the PUF. For example it was found that lignin could add rigidity, while starch or the addition of polyether (low rotation hinderance) could improve resilience.[54]

This is evident from Figure 2.32 where increased polyether content decreases the $T_g$, while a greater lignin content had the opposite effect.[89] The $T_g$ can also be controlled via the ICI as shown in Figure 2.33a. An increase in the ICI increases the cross-links preventing chain movement. Similarly, liquefied wheat straw was shown to behave as a cross-linking agent and also exhibited the same behaviour (Figure 2.33b).

![Figure 2.32: Relationship between the $T_g$ and PEG, as well as with the lignin fraction][89]

Morphology

The morphology of PUFs are known to correlate with many material properties. However, thorough characterization of the morphology through microscopy is rarely done because it is often plagued by complexities associated with getting reproducible data and selection of appropriate methods.[91] The typical cell geometry (tetrakaidecahedra) and morphology of a PUF are shown in Figure 2.34a and b.
Figure 2.33: a) Effect of ICI and b) Liquefied wheat content on Tg (Note: The ICI is quite high, but this is for a non-water blown PUF, it lacks the brittle hard-segment associated with urea formation due to water.)[90]

The cell shape is an important criteria. For example, the coarsening behaviour of a foam (change in cell size over time) is based upon the rate of diffusion of gas through the faces, and so the number of faces has the following relationship with cell expansion as described by the von Neumann growth law shown in Equation 2.6; where \( \frac{dV}{dt} \) is the change in volume with time, \( f \) is the number of faces on the cell, and \( \bar{f} \) is the average number of faces per cell (14), and \( C_2 \) is a constant. Therefore, if a cell has 14 faces it maintains its size, less than 14 it will shrink, and greater than 14 it will coarsen. Furthermore, changes in cell geometry impact the foam density, and density is the most important determinant of foam characteristics. Density of a foam is often described as the relative density: the ratio of the apparent density, \( p^* \) (calculated based on the foam) to the substrate density \( p_s \) (a plaque or film density). Equations relating the foam density to cell geometry for cells based on a tetrakaidecahedra geometry can be seen in Equations 2.7 and 2.8, for open and closed cells respectively; where \( t \) is the strut thickness, and \( l \) is strut length.[92] Cell morphology also encompasses several foam structural features as shown in Figure 2.34c, with typical values for a polyurethane foam, like the cell size and size distribution, strut lengths and thickness, membrane thickness, and open-closed cell content.

\[
\frac{dV}{dt} = C_2(f - \bar{f}) \tag{2.6}
\]

\[
\frac{p^*}{p_s} = 1.06\left(\frac{t^2}{l^2}\right) \tag{2.7}
\]

\[
\frac{p^*}{p_s} = 1.18\left(\frac{t}{l}\right) \tag{2.8}
\]
Although some features like strut thickness (SEM) and open-closed cell content (gas pycnometer) can be easily measured, something as simple as cell size and size distribution, which would be the most instructive, are quite difficult to measure. This is because samples produced via slicing can be at any angle through a cell. So even when cell size is uniform, cells will be sliced through the various faces of the polyhedral and yield an erroneous value. New techniques like x-ray micro-computed tomography (CT) use x-rays to map and reproduce a foam structure and generate a digital model, which can then be used to extract morphological features[93] and even model transport behaviour.[94]

This discussion of morphological features has so far not pertained to biomass based foams. The reason for this is that it is quite difficult to draw a relationship between the inclusion of a bio-polyol and its effect on the cell structure. Once the viability of biomass-based foams has been assessed more thoroughly, future work may delve deeper into the morphological ramifications. Often though, the impact of adding
a bio-polyol can have a drastic impact on the morphology that may be difficult to quantify, but easy to qualitatively observe. Their main impact likely stems from their diversity of alcohol groups which alter foaming reaction kinetics, as well as their increased viscosity making cell expansion limited due to the reduced flow behaviour. Qualitatively from Figure 2.35, SEM micrographs show that a change from 15 % wheat straw polyol to 30 % has ramifications including increased heterogeneity and increased open-cell content.[90]

![SEM micrographs showing morphology changes](image)

Figure 2.35: a) Scanning electron micrograph of a PUF made a) 15 % and b) 30% liquefied wheat straw [90]

### Compression Strength: Mechanisms and Theory

The characteristic stress vs. strain ($\sigma - \epsilon$) graph of a rigid foam can be seen in Figure 2.36. The first portion of the graph is the linear elastic region. In Equations 2.9 and 2.10 the relationships between density and elastic modulus can be seen.[92] The first term ($\rho^*/\rho_s$)$^2$ is based upon the elastic bending of struts. In a closed-cell foam there are additional mechanisms, the second term in 2.10 corresponds to cell membrane stretching, and the last term refers to the contribution from the pressurization of the enclosed gas. $C_1$ is a proportionality constant; $E^*$ is the elastic modulus of the foam; $E_s$ is the elastic modulus of the solid polymer; $p_0$ is the initial gas pressure $; \nu^*$ is Poisson’s ratio.

\[
\frac{E^*}{E_s} = C_1\left(\frac{\rho^*}{\rho_s}\right)^2
\]

\[
\frac{E^*}{E_s} \approx \phi^2\left(\frac{\rho^*}{\rho_s}\right)^2 + (1 - \phi)\frac{\rho^*}{\rho_s} + \frac{p_0(1 - 2\nu^*)}{E_s(1 - \frac{E^*}{E_s})}
\]

The next region which resembles a plateau involves the buckling of struts. This is a type of plastic deformation that is likely due to the weakness of the amorphous soft-segment regions in the polymer.

Within this region is where the compression strength is often measured at strains of 10% and 25%. Since compression strength has a power law relationship with density, and density of a foam is controlled by many factors (type/amount of blowing agent) the compression strength is often normalized for density. The normalized compression strength was based on equations in Ashby et al. that makes compression strength proportional to density for an open-cell foam as shown in Equation 2.11 and for a closed-cell
Figure 2.36: The typical stress-strain response of a rigid foam, image sourced from www.posterus.sk/?p=3923

foam in Equation 2.12.\cite{92} The first term in the equation, \( \frac{\rho_s}{\rho_s^*} \)^{3/2} relates to the formation of plastic hinges (struts buckling). The second term in Equation 2.12 refers to plastic stretching of the membrane. \( \frac{\sigma_{pl}}{\sigma_{ys}} \) is stress at which plastic collapse occurs divided by the yield stress; \( C_5 \) and \( C_n'' \) are proportionality constants; \( \frac{\rho^*}{\rho_s} \) is the foam density divided by the substrate (polymer) density; \( \phi \) is the volume fraction of polymer in the edges, \( \phi = 1 \) for open cell.

This illustrates one of the key difficulties in making comparisons of data since authors working on the same polyol could get differing results simply due to the formulation employed. Furthermore, the compressive behaviour of a PUF is a function of the foam morphology, the supramolecular polymer structure and the polymer molecular structure. In order to better understand how these influence the compressive behaviour the mechanisms of compressive failure will be discussed briefly.

\[
\frac{\sigma_{pl}}{\sigma_{ys}} = (C_5) \left( \frac{\rho^*}{\rho_s} \right)^{3/2} \quad (2.11)
\]

\[
\frac{\sigma_{pl}}{\sigma_{ys}} = (C_5) \left( \phi \frac{\rho^*}{\rho_s} \right)^{3/2} + C_n'' (1 - \phi) \left( \frac{\rho^*}{\rho_s} \right) \quad (2.12)
\]

As struts buckle the foam becomes denser and this densification leads to an increase in the compressive stress as the foam begins to approach the properties of a solid sample being compressed. This increase in the compressive strength is largely due to the absorption of energy from the cleaving and reformation of hydrogen bonds. In Figure 2.37a the reaction of a polyol with an isocyanate is shown, as well as the urethane linkage with the N-H group that acts as a proton donator, and the C=O group that acts as a proton acceptor, both essential for a polymer to form intra- and inter-molecular hydrogen bonding. The hydrogen bonding behaviour of the polyurethane dictates the phase separation or micro structure of the polymer as depicted in Figure 2.37b. Large molecular weight polyols will lead to amorphous regions that impart flexibility and this is referred to as the soft-segment. Short molecular weight polyols and the reaction of isocyanate with water lead to regions with very dense hydrogen bonding and even crystallinity. This imparts rigidity to the polymer and is referred to as the hard-segment. When the hard-segment is stressed it can absorb energy via the breakage of both inter- and intra-molecular hydrogen bonds as
depicted in Figure 2.37d and e. Rigid foams are highly resilient for this reason, they are able to absorb lots of energy throughout the deformation process.

Figure 2.37: a) the groups responsible for hydrogen bonding in a polyurethane; a) the effect of hydrogen bonding on polymer microstructure; a depiction of energy absorption through the rupturing of c) intra- and d)inter-molecular hydrogen bonds.

Conventional compression testing as described begins by probing the compressive modulus of the foam. The use of dynamic mechanical analysis through variation of temperature and frequency can provide insight into the viscoelastic behaviour of foams like the response of the storage and loss modulus. The storage modulus represents the elastic energy absorbed due to spring-like behaviour, while the loss modulus represents the energy absorbed through internal viscous motion like a dashpot. A measure for the damping, is $\tan \delta$, which is the loss modulus divided by the storage modulus. As temperature increases, the polymer expands in volume allowing the polymer chain components to move more easily, and thereby engage in dissipative dampening movements. Bending, rotating, stretching motions are depicted in Figure 2.38a, and are referred to as $T_\gamma$ transitions. When side chains and sections of the main chain begin movement this is referred to as $T_\beta$. Finally, as discussed previously, once the full main chain begins snake-like motion the glass transition is reached, $T_g$. Although, in a polyurethane with both hard and soft segments, the distinction between $T_\gamma$, $T_\beta$, and $T_g$ is often less obvious than the idealized plot shown in Figure 2.38b. This showcases the fact that there are a multitude of polymer chain structural features that determine the visco-elastic behaviour of the polymer, and ultimately the compressive behaviour. Although this section focuses on the compressive behaviour, it should be noted that the glass transition temperature also impacts thermal properties like the heat capacity, coefficient of thermal expansion, and molecular mobility (i.e. creep behaviour). A polymer that is nearby to its glass transition temperature will have greater free volume (increased coefficient of expansion) and therefore chains will have more mechanisms to absorb energy (increased heat capacity). These may be important design considerations, since a material will have to have the desired compression strength, throughout its operable temperature range. When producing a polyol from bark, there will be a great diversity of polymer chains introduced into the polyurethane network. Probing the dynamic and thermal response is therefore a useful method for understanding the changes that occur in the polymer network when a
biomass component like bark is introduced.

Figure 2.38: a) A schematic of the crankshaft model of a polymer chain, showing chain slippage, bending, rotating, stretching; and b) the thermo-viscoelastic response of a polymer [95].

Compression Strength: Summary of Biomass-based PUFs

As shown by the above literature review there are a multitude of parameters that can be varied that will play a role in determining the compression strength of a PUF. This makes comparison of literature results difficult, but a comparison can still be instructive. For example, Figure 2.39a presents a comparison of different methods for producing a polyol and the normalized compression strength at 10% strain. The normalized compression strength was based on equations in Ashby et al. that makes compression strength proportional to density for an open-cell foam as shown in Equation 2.11 and for a closed-cell foam in Equation 2.12. [92]
It is clear from this plot that foams produced via mixing tend to be very dense and that to achieve a low density foam biomass must be either liquefied through acid-catalyzed liquefaction or alkoxylation. Furthermore, the graph tends to show that PUFs made using alkoxylation occupy a similar density range as those from liquefaction, but have improved compressive behaviour. This is a trend echoed in the work reported herein.

In Figure 2.39b the above results are now arranged by biomass type. It can be seen that polysaccharides, lignocellulosic biomass, and lignin have the highest specific strength and that bark performs rather poorly. The reason for this is that previous work simply mixed the bark, but it will be shown in this work that when converted into a liquid polyol and then used to make a PUF that bark is quite promising as a feedstock.

The confidence ellipses plotted are centred at the average of the data set, and its radius is based upon the variance of the data, with a confidence interval of 80 %, meaning that 80 % of the data fits within the ellipse’s boundaries.

Summary

From the literature survey some important conclusions can be drawn:

- Bark is similar to wood in that it contains many lignocellulosic biopolymers, but differs in that it tends to have a high fraction of unique extractive compounds. These compounds tend to be of smaller molecular weight, phenolic in nature, and with hydroxyl functionality; all of which makes it suitable as a raw material for making a polyol.

- The conversion of biomass into a polyol, has been attempted on many feedstocks and under a variety of conditions and methods. Two of the most promising methods are the acid-catalyzed liquefaction in polyhydric alcohol solvents and the base-catalyzed alkoxylation.

- The inherent diversity in biopolymers and their subsequent modification during the conversion process can make polyol characterization a challenge. For this reason, the characterization of bio-based polyols tends to be quite superficial, with papers focused on mechanical properties of the foam. There are even fewer attempts to link foam properties to polyol structure.
Figure 2.39: A comparison of normalized compression strengths at 10% strain of foams made by a) mixing biomass into a polyol, alkoxylation, or liquefaction; and of PUFs made only from b) bark or tannin; ‘n’ is the number of papers used to construct the dataset; the normalized compression strength is $\frac{\sigma}{\rho}$ at 10% strain as shown in Gibson and Ashby et al. [92]
Chapter 3

Materials and Methodology

The materials used and their purchasing information are found in section 3.1; procedures for bark conversion are found in section 3.2.1; bark-polyol characterization is found in section 3.2.2; residue characterization is found in section 3.2.3; and foam characterization is found in 3.2.4. Some procedures and material preparation differ based on the chapter.

3.1 Materials

- Purchased from Caledon Laboratories:
  - chlorobenzene, chloroform, dimethylformamide, dioxane, ethanol, glycerol, hexanes, hydrochloric acid, potassium hydroxide, pyridine, sodium hydroxide, sulphuric acid, tetrahydrafuran, toluene, xylene,
- Purchased from Fisher Scientific:
  - PEG-400
- Purchased from Sigma Aldrich:
  - 2,4-dimethylpentanone, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, acetyl acetone, benzyol chloride, celite 545, chloroform-d1, chromium (III) acetylacetonate, cholesterol, cyclohexanone, dimethylsulfoxide-d6, imidazole, phthalic anhydride, polyethylene glycol (Mw.2050), polypropylene glycol 425, propylene oxide, triethyelene glycol, and tripropylene glycol,
- Provided by Huntsman:
  - RUBINATE M polymeric MDI (pMDI) and two amine catalysts: N,N-dimethylcyclohexylamine (DMCHA) and Pentamethyldiethylenetriamine (PMDETA) (from the JEFFCAT catalyst product line). Polyols: G30-650, Jeffol PPG 2000, FX-31-167, FE 12-60, and SD-361.
- Provided by Air Products Inc. Surfactant DABCO DC5604
- Bark: mountain pine beetle infested lodgepole pine (*pinus contorta*) bark was supplied by FPInnovations.

Chapter 4: The bark was ground into a bark powder using a Wiley mill and then passed through a 70 mesh (0.211mm) sieve.
Chapter 6: The bark was ground into a bark powder using a Wiley mill and then passed through a 70 mesh (0.211mm) sieve. The powder was de-waxed through soxhlet extraction with hexanes for four hours, after which it was dried in an oven over night at 70 °C.

Chapter 5 and 7: The bark was ground into a bark powder using a Wiley mill and then passed through a 60 mesh (0.251mm) sieve. The powder was de-waxed through soxhlet extraction with hexanes for four hours, after which it was dried in an oven over night at 70 °C. This fraction was shown in previous work to mainly contain terpenes and unwanted fatty acids. The moisture content was determined using a Denver Instruments IR-200 Moisture Analyzer, and found to be 8 %.

3.2 Methods

3.2.1 Bark Conversion

Liquefaction

Chapter 4 and 6: The experiment was done at three different temperatures (90 °C, 130 °C, and 160 °C), and produced polyols P90, P130, and P160; respectively. Polyethylene glycol (PEG) (37.5 g, 30 g, 38 g), glycerol (G) (1.99 g, 1.59 g, 2.02 g), sulfuric acid (1.99 g, 0.80 g, 0.67 g), bark (37.5 g, 15 g, 12.67 g), and a co-solvent (water-200 mL, xylene-30 mL, none) were added to a flask. The flask was then heated for two hours at the respective temperature under nitrogen. After which NaOH (0.814 g, 0.325 g, 0.275 g) was added to neutralize the sulphuric acid. Next, the solutions were diluted through addition of a dioxane:water (8:2) solution (400 mL), and allowed to stir overnight. The solutions were then centrifuged at 1500 RPM for 15 minutes, filtered, and washed with dioxane-water (8:2). The solid residues were then dried at 60 °C to determine the amount of residue.

\[
\%\text{Residue} = \frac{\text{Weight of Residue}}{\text{Weight of biomass}} \times 100
\]

The ratio of bark to biomass was used (as shown in 4.1) as a control variable to ensure that all the polyols had roughly a bark-content of 20 % even though their yields were different. Therefore, comparisons would be easier to make since the bark component was roughly equal in all the polyols. An iterative process was used, where the biomass ratio was changed and liquefactions were repeated till the bark content values of the three temperature conditions were similar.

Chapter 5: Liquefactions were conducted at 130 °C to produce bark-based polyols. A polyhydric alcohol (7.2 g), glycerol (0.8 g), sulfuric acid (0.4 g), bark (4 g), and a co-solvent (20 mL) were added to a flask fitted with a condenser. The polyhydric alcohols used are listed in Table 5.1 and the co-solvent used was xylenes. The flask was then heated for one hour at 130 °C under a nitrogen environment. Next, the solution was diluted with a dioxane-water (8:2) solution (80 mL), and then neutralized using a 5 M sodium hydroxide solution. The solutions were then filtered and washed with dioxane-water (8:2). The water and dioxane were then removed through rotary evaporation for a sufficient period to ensure maximal removal of water. An additional set of liquefactions were done using PEG-400 as the polyhydric alcohol, and the co-solvent was varied (chlorobenzene, acetyl acetone, cyclohexanone, dimethylformamide, and 2,4-dimethylpentanone).
Oxypropylation

The reactions were performed in a 600 mL Parr non-stirred reactor, with a pressure gauge, thermometer, and heated with an electric mantle. It was reported in the literature that an ethanol-KOH pre-treatment improves activation of the biomass hydroxyl groups and allows the KOH catalyst to be evenly distributed.[69] Potassium hydroxide (240.6 mg) dissolved in ethanol (40 mL) and bark or alkaline extracts of bark (15 g) were added to the vessel. The vessel was filled with nitrogen to 50 PSI, and heated to 100 °C, and then held for 1 hour. The pressure valve was released and kept for another 0.5 hour to allow the vessel to cool. The pretreated bark was dried in an oven overnight at 70 °C to evaporate the ethanol. The pretreated bark (15 g) and PO (50 mL) were mechanically stirred and then added to the vessel and heated to 180 °C. The total reaction time was 2 hours, which included heating from room temperature to the set temperature of 180 °C. After it had cooled to room temperature, chloroform (375 mL) was added. The solution was neutralized with 1M HCl, filtered using Celite 545 as a filtration aid, and washed with chloroform. The filtrate was rotary evaporated and produced the polyols from bark (OP-B) or the alkaline extracts of bark (OP-AB). The solid residues were dried at 60 °C in an oven to determine the biomass conversion yield.

\[
\text{Biomass Conversion Yield (\%)} = \frac{(\text{Weight of Biomass} - \text{Weight of Residue})}{\text{Weight of Biomass}} \times 100
\]

\[
P(t=2\text{hr}) = \frac{N_{PO,t=2\text{hr}} - N_{PO,t=0\text{hr}}}{RT} \times 100
\]

Where \(N_{PO,t=2\text{hr}}\) is the moles of PO in the reactor at the end of the reaction; \(N_{PO,t=0\text{hr}}\) is the moles of PO added to the reactor; \(P(t=2\text{hr})\) is the final pressure in the reactor, \(P_{N_2}\) is the amount of nitrogen used as backfill and corrected to 180 °C; \(V_{\text{Reactor}}\) is the volume of the reactor; \(R\) is the ideal gas constant; and \(T\) is the temperature which was 180 °C; \(p\) is the monomer conversion.

Bark Extraction with 1 % NaOH

This procedure was modified from the work of Vazquez,[31] using a solid to liquid ratio of 1:10, but using only a 1% NaOH extraction. The reaction was carried out in a 2 L round bottom flask at 90 °C with mechanical stirring. 1% NaOH (750 mL) and bark (75 g) were added and allowed to mix for 2 hours. The flask was removed from the water bath and allowed to cool. The slurry was filtered using Celite 545 as a filtration aid and the residues were washed with water. The filtrate was neutralized using 1M HCl and filtered again. The solution was oven dried at 70 °C. The dried extract was then ground using a mortar and pestle till it could pass a 40 mesh sieve (422 um). The alkaline extraction yield from bark was 45.4 %.
3.2.2 Polyol Characterization

Viscosity and Gel Permeation Chromatography

Chapter 4: The viscosity was measured using a Brookfield Synchro-electric viscometer and was an average of three measurements.

Chapter 7.5: A BYK DV-E rotational viscometer was used with a temperature controlled sample holder at 25 °C.

Chapter 4: GPC was done using THF as a solvent on system consisting of a Waters 2695 Separations Module, Waters 2998 Photodiode Array, and Styragel HR4E and 5E columns in series. The GPC was calibrated using the UV detector and polystyrene samples standards. The samples were prepared based on the procedure by Salanti et al.[97]. Polyol (125 mg), pyridine (6.7 mL), and benzoyl chloride (77 uL) were stirred in a vial for two hours, then diluted with a 1:3 water-ethanol solution (50 mL), then stirred for five minutes, followed by two toluene (50 mL) liquid extractions. The toluene was rotary evaporated, the residue dissolved in THF, and passed through a filter prior to analysis. The amount of benzoyl chloride was in excess to the moles of OH groups (1.1:1), based upon an OHV of 280 mgKOH/g as an upper estimate from the esterification titrations done in this work.

Chapter 7: Derivitization of the polyols was not needed for alkoxylated samples due to their improved solubility in THF. The GPC was calibrated using the refractive index detector and a combination of polyethylene oxide and polystyrene samples from 156,000 Da to 580 Da were used as calibration standards.

Fourier Transformed Infrared Spectroscopy

Chapter 4: Analysis was performed on a Bruker Tensor 27 FTIR spectrometer using sodium chloride discs with the liquid polyol sample sandwiched in between.

Hydroxyl value (OHV) determination

The OHV was determined by the standard pthalic anhydride method[98] and by the phosphorous NMR method.[99, 100] The reactions of both are shown in Figure 3.1.

![Figure 3.1](image)

Figure 3.1: a) The reaction of pthalic anhydride with an alcohol to produce an equivalent amount of carboxylic acid that can be titrated and the b) derivitization reaction of a phosphorous containing reagent with an alcohol to produce a phosphorous linkage whose $^{31}$P ppm shifts correspond to the type of alcohol that was present.
The hydroxyl value (OHV) was determined by the standard esterification method using phthalic anhydride.[98] Polyol (1 g) and the phthalation reagent (25 mL) were heated at 100 °C for fifteen minutes, cooled to room temperature, pyridine (50 mL) was added, followed by water (10 mL), and then titrated with 0.5M NaOH to its equivalence point. The phthlation reagent was a solution of phthalic anhydride (41.43 g) and imidazole (6.43 g) in pyridine (250 mL). Where S and B₁ are the mL at the equivalence point of the sample and blank (no polyol), respectively; N is normality of NaOH; and W is the weight of the sample; OHV is the hydroxyl value in mgKOH/g of sample.

\[ OHV_{PA} = \frac{(B_1 - S)(56.1)(N)}{W} \]

\(^{31}\)P-NMR analysis was done on a Varian Mercury 300 spectrometer using a 23 kHz spectral width with an acquisition time of 1.8 s, relaxation delay of 10 s, observation pulse of 30 µs, and 256 scans. Samples were prepared based on the phosphitylation method using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP).[99, 100] A stock solution of pyridine-deuterated chloroform (1:1.6, w/v) was prepared and used to prepare a relaxation solution using chromium (III) acetylacetonate (5 mg/mL), as well as a standard solution of cholesterol (5 mg/mL). All three were dried with molecular sieves. The samples were prepared by mixing the liquid polyol (15 mg), relaxation solution (0.1 mL), standard solution (0.1 mL), and stock solution (0.8 mL). Finally, TMDP (0.1 mL) is added, shaken vigorously, and then transferred to an NMR tube for analysis. All spectra used a line broadening of 1 Hz, were calibrated to the water peak at 132.2 ppm, and had a peak for excess TMDP to ensure that all reactive species had been completely phosphitylated. The OHV values were an average of three samples and were integrated relative to the cholesterol standard. The water content of the polyol required a blank sample to be run to negate the amount of water absorbed from the environment and solvents.

**Nuclear Magnetic Resonance Spectroscopy**

Chapter 4: Carbon and proton NMR were done on a Varian 600 spectrometer in DMSO-d₆ at a concentration of 100 mg/mL. \(^{13}\)C-NMR measurements had a 0.1 s relaxation delay, pulse angle of 45°, acquisition time of 1.42 s, spectral width of 35 KHz, and 20K scans. \(^1\)H-NMR used a 1 s relaxation delay, pulse angle of 30°, acquisition time of 1.7 s, spectral width of 9600 Hz, and 64 scans. Both were calibrated using TMS.

Chapter 6: \(^{13}\)C-NMR and \(^1\)H-NMR were performed on a Varian 400 spectrometer in DMSO-d₆ at a concentration of 100 mg/mL. C-NMR measurements had a 0.2 s relaxation delay, pulse angle of 30°, acquisition time of 1.2 s, spectral width from -15 to 235 ppm, and 20K scans. \(^1\)H-NMR used a 1 s relaxation delay, pulse angle of 30 °, acquisition time of 1.7 s, spectral width from -2 to 16 ppm, and 64 scans. Both were calibrated and normalized using the solvent peak for DMSO.

**Assessment of Degradation and Aromatic Content** From the proton spectra, the following areas were integrated to represent the amount of degradation and the aromatic content. The solvent residual proton peak in deuterated DMSO (2.45 - 2.55 ppm) was used as the standard for integration. The degradation peaks integrated consisted of the L5 (2.05 - 2.15 ppm) methine peak for levulinic acid and the F1 (8 - 8.5 ppm) methyl peak for formic acid as shown in Figure 5.6. The aromatic region was integrated from 6 - 8 ppm. The integrated values were divided by the values from the P-2-200 (PEG-400) sample to provide a relative comparison. PEG-400 is a common glycol and polyhydric alcohol used in liquefactions, and served well as a basis for comparison.
Homopolymer Content

The polyols OP-B/OP-AB (10 g) were added to a flask with hexanes (150 mL) and refluxed, and then an extraction was performed twice for 2 hours each. The hexane solutions from the two extractions were combined and the solvent was removed through rotary evaporation to produce the homopolymer. The low solubility of low-molecular weight glycols in hexane may result in an under-estimation of the homopolymer content.

\[
\text{Homopolymer} (\%) = \frac{\text{Weight of Homopolymer}}{\text{Weight of Polyol}} \times 100
\]  

(3.3)

3.2.3 Residue Characterization

Elemental Analysis

Elemental Analysis was performed on a 2400 Series II CHNS Analyzer to determine the carbon content of the residue. All values were made relative to the carbon content of the initial bark. A value of greater than one indicates that the residue consists of condensation products that have increased in carbon content due to the release of oxygen as water. This is based on the method used by Heitz et al. where a carbon to oxygen ratio was used.[101]

Residue Analysis

The extractives content of the residues was determined by the TAPPI standard method T-204 cm97: Solvent Extractives of Wood and Pulp; however benzene was substituted with toluene. The acid insoluble lignin content was determined by the TAPPI standard method, T-222 om-02: Acid-insoluble Lignin in Wood and Pulp. The acid soluble lignin content was found to be negligible and it has been reported to be less than 1 % for softwood species.[102]

3.2.4 Formulation, Foaming, and Foam Characterization

Formulation and Foaming

Foams were prepared at two scales to produce a foam-bun and a cup-foam, where 5 g and 22 g of polyol were used respectively. Relative to the weight of the polyol, 0.25% DMCHA, 1.25% PMDETA, 2% surfactant, and 5% water as the blowing agent were stirred together with the polyol, followed by sonication for five minutes. Foam Bun: The polyol solution was poured into a cup, and the pMDI is added while on a scale to ensure the isocyanate index is approximately 1.1. The cup was then mixed at high speed using an overhead mixer for ten seconds, poured into a mould, and allowed to foam. The samples were kept overnight to cure before de-moulding and cutting.

Foaming Kinetics

To measure the foaming kinetics the foams were prepared at a smaller scale and allowed to foam within the cup. The temperature and height were measured using a custom device consisting of an Arduino Dueilanove programmable microcontroller circuit board, a 10k thermistor as a temperature sensor, and an infra-red distance sensor (Sharp GP2D120).
Thermistors can be used within a temperature range of -90 to 130 °C, and their behaviour can be described by the Steinhart-Hart Equation in Equation 3.4.

\[
\frac{1}{T} = A + B \ln(V) + C \ln(V)^3
\]  

(3.4)

A 10K thermistor was shown to have the following values: \(A= 0.001129148\), \(B=0.000234125\), \(C=0.000000876741\).

V is the voltage measured in volts, and T is the temperature in K.

Data was found on: http://www.eidusa.com/Electronics_Kits_TEMP_THERMISTOR_1.htm

The IR-sensor can be used to measure distances from 4 to 30 cm, but has a non-linear response that was linearized by Equation 3.5.

\[
D = \frac{2914}{(V + 5)} - 1
\]  

(3.5)

D is the distance in cm and V is the voltage in volts.

Data was found on: http://www.acroname.com/robotics/info/articles/irlinear/irlinear.html

The device was programmed based upon open-source code. After mixing for ten seconds the height sensor was clamped above the cup, and the thermistor cable was immersed into the foaming polymer; this point was considered the starting point or time zero of the analysis. The foaming kinetics were also assessed using the more qualitative approach based upon the start of rise, full cup, gel, and tack-free times. Start of rise is the time at which foaming occurs; full cup represents the time at which the foam reaches the rim of the cup; the gell time represents the time at which a strand of polymer can be drawn from the foam; and the tack-free time is the time at which the surface is no longer sticky. The timer was started at the beginning of mixing which was done for ten seconds.

**Thermo-gravimetric analysis (TGA)**

Analysis was done on a TA instruments Q50 TGA at a heating rate of 10 °C/min under nitrogen.

**Attenuated Total Reflectance Fourier Transformed Infrared Spectroscopy**

Chapter 6: Attenuated total reflection spectroscopy (ATR) was performed on samples prepared from bun-type foams. They were compressed using a press prior to analysis on a Bruker Tensor 27 FTIR spectrometer. Forty scans were taken, each with a resolution of 4 cm\(^{-1}\).

**Degree of Swelling and Soluble Fraction**

The degree of swelling and soluble fraction were determined based upon the procedure by Campanella et al.[88] Values were reported as an average of three measurements.

**Morphology Characterization**

The closed-cell content was determined using an Ultrapycnometer 1000 by Quantachrome Instruments using nitrogen gas. The closed-cell content was determined using the following set of equations:
\[ O_v = \frac{V - V_{SPEC}}{V} \times 100 \] (3.6)

\[ W_v = \frac{m}{\rho_{SOLID}(V)} \times 100 \] (3.7)

\[ C_v = 100 - O_v - W_v \] (3.8)

Where \( O_v \) is the percentage of open-cell content, \( V \) is the geometric volume as determined by calipers (g/cm\(^3\)), \( V_{SPEC} \) is the enclosed volume inaccessible to the inert gas obtained from the pycnometer, \( W_v \) is the percentage of volume occupied by cell walls, \( m \) is the mass of the specimen (g), \( \rho_{SOLID} \) is the density of solid polyurethane obtained from pycnometry measurements of a ground PUF (g/cm\(^3\)), and \( C_v \) is the percentage of closed-cell content.

The cell morphology was studied using a stereo AMScope optical microscope using an AMScope MT1000 camera. Images were edited in ImageJ to add scale bars, and in Photoshop CS2 to desaturate and enhance contrast in the images. The foam density reported is based upon the bulk density of the bun-foams and is an average of four measurements.

**Mechanical Testing**

Chapter 6: Compression testing was done on an Instron tensile tester at a cross-head speed of 2.5 mm/min. Samples were cut from the bun foams into rectangular prisms of approximately 5 x 5 x 3 cm, compressed in the rise direction, and were done in triplicate.

Chapter 7: Compression tests were done on an Instron tensile tester with compression platens that moved at a cross-head speed of 2.5 mm/min. Samples were cut from the cup foams into rectangular prisms of approximately 4 x 4 x 3 cm, compressed in the rise direction, and was done in duplicate. The foam density reported is based upon the bulk density. Each sample’s volume and mass were measured, and the reported value is the average of the two samples.
Chapter 4

The Effect of Liquefaction Temperature on Polyol Structure

The following work has been adapted from the journal ACS Sustainable Chemistry & Engineering:


4.1 Introduction

Previous work done on bark-based polyols have relied on physically mixing a bark powder into a polyol or through harsh liquefactions to optimize conversion yield. However, without thorough polyol characterization the state of degradation, i.e. the loss of functional groups and cleavage into small molecular weight fragments, has not been assessed.

Hartman[103] and Ge et al.[104] made bark-based PUFs by mechanically mixing bark or tannin extractives into polyols,[104, 105, 106, 107] and found the bark-based PUFs were able to biodegrade.[55] Even though liquefaction of bark was also used to produce PUFs, the prior work focused mostly on the foam properties with limited attempts to systematically investigate the impact of the liquefaction conditions on properties of the bark-based polyols.[60, 54] In some studies, bark was liquefied at high temperatures using the bisulfite method to produce polyurethane foams and films.[61, 62] At 250 °C these polyols were shown to contain tannin degradation products featuring phenolic compounds with varying degree of acetyl, methyl, and hydroxyl functionalities.[63]

Yamada et al.[64, 65] and Jasiukaityte et al.[59] studied the liquefaction of cellulose and wood and found that the liquefaction at high temperatures, such as 150 °C, was too harsh and resulted in substantial degradation of cellulose to levulinate esters. At this temperature, lignin was modified by glycols undergoing condensation reactions with the phenolic hydroxyls to produce aliphatic hydroxyl groups.[66] However, their studies did not look into the liquefaction behaviour of wood and cellulose at lower temperatures. Since properties of the polyurethane foams depend on the molecular structure and properties of the polyols, it is crucial to determine how the liquefaction conditions affect key characteristics of the bark polyols.
In this study bark liquefaction reactions were carried out under mild, medium, and high temperatures to study the impact of the liquefaction temperature on the bark-based polyols. The three temperature levels are 90 °C, 130 °C, and 160 °C. At the mildest liquefaction temperature of 90 °C with water as the co-solvent, the reaction was a hybridization of a solvent liquefaction with a hot-water extraction, with the latter being the method commonly used for condensed tannin extractions. The liquefactions at 130 °C and 160 °C used xylene as a co-solvent to mimic the method used to determine the extractive’s content. The highest liquefaction temperature of 160 °C was chosen to produce a polyol containing highly degraded bark-biopolymers. The medium liquefaction temperature of 130 °C represented an intermediate condition where some levels of bark polymer degradation were expected. All the liquefactions used were a blend of PEG-400 and glycerol (95:5, %w/w).

### 4.2 Results and Discussion

**Yield and Composition**

In this study a 20 wt.% biomass fraction in the bio-based polyols was set as the target for selecting liquefaction conditions at different temperatures to facilitate the comparison. As a result, the polyhydric alcohol solvent to bark ratio was modified to ensure a bark contents close to 20 wt.% as shown in Table 4.1.

| Table 4.1: Comparison of bark liquefaction conditions |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Polyol Temperature Bark Ratio | PEG-G Bark Ratio | Bark Content (%) | Residue (%)     |
| (°C)                           | (%)             |                 |                 |
| P90                            | 90              | 1.05            | 17.6            | 77.5            |
| P130                           | 130             | 2.10            | 18.1            | 53.4            |
| P160                           | 160             | 3.16            | 20.1            | 20.4            |

Characterization of the polyol can be quite complex. For that reason, the solid residues from the reaction were characterized, and from that the composition of the polyol can be inferred through comparison to the pristine bark. From Figure 4.1, it can be seen that at 90 °C approximately half of the bark extractives as well as some accessible polysaccharides, like hemi-cellulose and amorphous cellulose, were extracted from the bark. At 130 °C nearly all of the bark extractives and half of the holocellulose in bark were liquefied. At temperatures below 160 °C lignin was not extracted from bark. By scaling the residue composition with the residue yield, it was possible to identify that the rise in lignin content from 22 % in the original bark to around 25 % in the unliquefied residues at 90 °C and 130 °C might be due to the production of tannin condensation polymers known as phlobaphenes. Interestingly, a small amount of extractives remained in the residues after liquefaction at even the highest temperature. This could be due to the limited diffusion through the bark cell walls during the liquefaction process. It should be noted that the residue amounts are relatively higher than those reported in the literature for other types of biomass. Phenolic compounds are known to easily recondense into insoluble large molecular weight lignin-based polymers, thereby increasing the amount of residues. Even though glycerol was found to retard the recondensation reactions,[108] a high glycerol content was not desirable since it could also lead to highly brittle foams.
Figure 4.1: The effect of temperature on the residue composition and the yield is shown. The first bar is the amount of bark that is successfully liquefied. The unliquefied bark residue values are broken down into their biopolymer fractions. This indirectly suggests which compounds were liquefied to produce the bark-based polyols.
Hydroxyl value (OHV) and $^{31}$P-NMR spectroscopy

In the literature the characterization of liquefied biomass polyols has relied upon the standard esterification-phthalic anhydride method to determine the hydroxyl value.\[98\] This method was shown to be comparable to other methods for the determination of OHV,\[109\] although inaccuracies have been observed when solvents other than pyridine were used to analyze sterically hindered alcohols and phenolic alcohols.\[110\] Regardless, phenolics can escape the downstream reaction with an isocyanate,\[111\] and therefore alternative methods are needed to characterize bark-based polyols to provide insight into the quantity of each type of hydroxyl groups present. A $^{31}$P-NMR method, based upon a hydroxyl group reacting with a phosphitylation reagent, is able to quantitatively determine the type of hydroxyl group and the water content.\[112\] The phosphitylation agent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP), has been used quite extensively for analyzing lignin,\[113\] as well as carbohydrates,\[114\] but has not been applied previously to characterize liquefied biomass polyols.

The OHV values obtained by the phthalic anhydride method in Table 4.2 showed that all the three polyols were similar in their hydroxyl content and possessed a suitable OHV for making a PUF. The values obtained by the PA method were consistent to those derived from the phosphorous NMR method. However, the phosphorus NMR method provided more insight. The results from the $^{31}$P-NMR were summarized in Table 4.2, as well as a representative spectrum in Figure 4.2b. The spectra were similar in that the PEG ($P_2$) and the glycerol hydroxyl peaks ($G_2; G_1$) were the dominant features.\[115\] Furthermore, it was anticipated that with lignin and condensed tannin extractives, considerable amounts of phenolic groups would be observed in the spectra. However, quite surprisingly this was not the case. Instead aliphatic hydroxyls accounted for most of the hydroxyl groups. The loss of the phenolics may be due to their condensation with the PEG and the glycerol in solution, analogous to a chain-extension. Liquefaction converted the sterically hindered phenolics into an easily accessible primary alcohol. This is of relevance since variation in the hydroxyl type will alter reactivity and kinetics. When using TMDP, a primary alcohol is at a higher ppm shift than a secondary alcohol. Although these regions are not strictly defined it would appear that the P90 aliphatic region had an additional primary alcohol and a greater diversity of secondary alcohols compared to both the polyols P130 and P160. Although specific assignments were not made, this pattern is consistent with the structure of a sugar, shown to be present in the P90 polyol from the carbon NMR results.

Table 4.2: Hydroxyl values via the phthalic-anhydride (PA) and phosphorus method ($^{31}$P), and viscosity of the three polyols

<table>
<thead>
<tr>
<th>Polyol</th>
<th>OHV (mgKOH/g) PA</th>
<th>$^{31}$P OHV (mgKOH/g)</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P90</td>
<td>265</td>
<td>228±61</td>
<td>142.5</td>
</tr>
<tr>
<td>P130</td>
<td>275</td>
<td>235±60</td>
<td>800</td>
</tr>
<tr>
<td>P160</td>
<td>231</td>
<td>331±26</td>
<td>1650</td>
</tr>
</tbody>
</table>
Table 4.3: Quantitative $^{31}$P-NMR of Liquefied Bark Polyols

<table>
<thead>
<tr>
<th>Region (ppm)</th>
<th>P90 (mgKOH/g)</th>
<th>P130 (mgKOH/g)</th>
<th>P160 (mgKOH/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic (148-146)</td>
<td>205±67</td>
<td>261±53</td>
<td>316±12</td>
</tr>
<tr>
<td>Phenolic (143-137)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Water (132±16.2)</td>
<td>0</td>
<td>0</td>
<td>134±17</td>
</tr>
<tr>
<td>Water (wt%)$^a$</td>
<td>0</td>
<td>0</td>
<td>2%</td>
</tr>
</tbody>
</table>

$^a$ Water content for P90 and P130 were negligible once corrected with blank

Figure 4.2: (a) Structure nomenclature for NMR assignments of i-PEG, ii-glycerol, iii-levulinate esters, iv-formic esters, v) glucose; (b) the $^{31}$P-NMR spectrum of P90 showed that only aliphatic hydroxyls and water are present, as the phenolic region had no visible peaks (also representative of P130 and P160); (c) $^{31}$P-NMR spectra of the aliphatic hydroxyl region showed the preservation of sugar hydroxyls in P90, in contrast to P160 and P130.
Viscosity and GPC

Increasing the liquefaction temperature also increased the viscosity of the polyols as shown in Table 4.2. Although the hydroxyl content varied slightly among the samples, it was clear that the molecular structures of the three polyols were different. This was verified by the GPC data shown in Figure 4.3. The poor solubility of the polyols in tetrahydrufuran required a benzoylation derivitization reaction prior to analysis, as described in the method section. All of the polyols featured broad molecular weight distributions below 10,000 Da. P90 had a large fraction of low molecular weight (LMW) compounds below 580 Da that indicates the presence of depolymerization products, while at higher temperature in P160 the LMW fraction is likely degradation products. Since these LMW compounds are at the low end of the GPC’s ability to separate and analyze future work may utilize a fractionation to separate these compounds. This would enable their formation to be better understood, but also provide an avenue to upgrade the quality of their polyol via their removal. At high molecular weight tail signified polymers formed from the condensation of phenolics.

The LMW compounds may also include partially benzoylated sugars and tannin degradation products as steric reasons would prevent complete derivatization. The low temperature used to produce P90 resulted in degradation exceeding the rate of recondensation. Similarly, P160 showed that the rate of degradation of sugars and lignin fragmentation exceeded the rate of recondensation; despite the large molecular weight fraction approaching 10,000 Da. In contrast, P130 showed a balance, where the molecular weight profile featured a very broad plateau with shallow troughs. The great variation among these polyols demonstrated the need for a thorough characterization of the polyols as the molecular weight distributions were rarely obtained for liquefied biomass polyols previously, despite the molecular weight being a key characteristic of polyols.

Figure 4.3: GPC profiles of P90, P130, P160 polyols. The chromatogram showed that a large fraction was low molecular weight compounds. Also, the large molecular weight tail became more pronounced with higher liquefaction temperature.
Carbon and Proton NMR

The carbon NMR spectra were dominated by the PEG polyhydric alcohol solvent carbons as shown in Figure 4.4a: the ether carbons within the PEG (P₁), the PEG OH (60.1), and the primary and the secondary alcohols of the glycerol, respectively (G₁, G₂). Upon comparison of the three polyols, P130 and P160 were similar, while P90 was quite distinctive. The liquefaction conditions of P90 produced the only polyol to show peaks in the aromatic region. The peaks in the 140-150 ppm region were consistent with a methoxy or an aromatic ether, such as a condensation product between a phenolic group and a PEG or glycerol molecule. Tannins degrade into a variety of structures under alcoholysis.[67] Here, large variation in the structure could have led to the aromatic carbon peaks being too scattered and too weak to be significantly above the signal to noise threshold in the spectrum. This could also hold true for the aromatic peaks in the other polyols, where the large ppm shifts for a diversity of substitutions might have resulted in peaks hidden by the noise.

Furthermore, only the liquefaction conditions used for P90 showed the presence of a sugar. Assignments of the sugar carbons can be difficult due to the multitude of peaks from the anomeric effect, and whether or not C₁ and C₄ are involved in the glucosidic bonds. However, peak assignments could be made for C₁, C₄, and C₆ as shown in Figure 4.4; as well as the peaks observed in the region typical of C₂, C₃, C₄, and C₆. Under the harsher conditions used to produce P130 and P160 the sugars had degraded into formate and levulinate esters. The characteristic carbonyl peaks of a levulinate ester (L₁, L₄) and a formic ester (F₁) can be seen in Figure 4.4b, as well as the methylene (L₂, L₃) and methyl (L₅) carbons. These results are further corroborated by the proton NMR spectra in Figure 4.5.

![Figure 4.4: Carbon NMR spectra of P90 and P160](a) Both have intense peaks corresponding to the carbons from the PEG and the glycerol; (b) P90 featured the peaks characteristic of a sugar and an aromatic compound, while P160 and P130 exhibited the peaks consistent with the presence of a formic ester and a levulinate ester.
Chapter 4. The Effect of Liquefaction Temperature on Polyol Structure

Figure 4.5: Proton NMR spectra of P160 showing peaks consistent with the presence of sugar degradation products consisting of formic esters and levulinate ester

Fourier Transformed Infrared (FTIR) Spectroscopy Analysis

The FTIR spectra of the polyols are shown in Figure 4.6, where the dominating feature in all three polyols was the broad hydroxyl peak at 3400 cm$^{-1}$, implying a significant amount of hydrogen bonding. The strong peak at 2870 cm$^{-1}$ corresponded to a C-H bond of an indiscernible origin. However, its shoulder that was more pronounced in P90 and P130 was indicative of the O=C-H stretch of an aldehyde. It was also observed that there was a peak at 1960 cm$^{-1}$ that could be attributed to a carbon double bond originating from fatty acids, triglycerides, terpenes, and stilbenes; all being typical bark extractive components. One significant difference among the polyols was the change in intensity of the peaks in the double bond region (2000-1500 cm$^{-1}$). The carbonyl peak at 1730 cm$^{-1}$ is characteristic of aldehydes, ketones, esters, and carboxylic acids. This peak’s intensity increased with increasing liquefaction temperature. This result was consistent with the carbon NMR analysis that showed the presence of levulinate and formic esters in P130 and P160.

Figure 4.6: The FTIR Spectra of P90, P130, and P160 polyols
4.3 Conclusions

Through liquefaction at three different temperatures and characterization of the resultant polyols, the effect of the liquefaction temperature on the structure and composition of the bio-based polyols was studied. At 130 °C and 160 °C holocellulose was converted into levulinate and formic esters in the liquefied bark fraction; while at 90 °C sugars were still present. This shows that at higher temperature the polyol contains many low functionality degradation products. From residue composition analysis it was found that high temperatures were needed to extract lignin, 160 °C, while at 130 °C lignin remained in the residue. Other phenolics (extractives) were easily extracted. Their aromatic structures were kept intact; however the $^{31}$P-NMR analysis showed that the phenolics were converted to aliphatic alcohols via condensation reactions with the PEG/Glycerol. This is beneficial since phenolic alcohols produce weak urethane linkages. Finally, the GPC analysis showed the polyols duality by containing both low molecular weight degradation products and high molecular weight recondensation polymers. The presence of low molecular weight fragments appeared in all polyols; however with increasing liquefaction temperature the extent of condensation reactions increased. This was manifested most in the sample that was liquefied at the highest temperature, which consequently had the most viscous polyol and the highest molecular weight tail stretching to 10000 Da.

These results help elucidate some of the complex changes to bark biopolymers and condensed tannins during a liquefaction reaction. Understanding the effect of the liquefaction conditions on the bark polyols composition and molecular structures would be beneficial for utilization of these bark-derived bio-polyols.
Chapter 5

The effect of liquefaction solvents on the properties of bark-based polyols

The following work has been adapted from the journal of Sustainable Chemistry & Engineering:


5.1 Introduction

In chapter 4, bark was liquefied at 90 °C and 130 °C. It was found that the polyols did not contain lignin, but only accessible sugars (amorphous cellulose / hemi-cellulose) and extractive-like compounds (tannins, terpenoids, lignans).[117] The polyol produced from the liquefaction of bark at 130 °C produced foams with compression strength comparable to control foams (Chapter 6). But, the presence of degradation products / low functionality compounds in the bark-based polyols may have negatively affected both the closed-cell content and network formation.[118] Therefore, if the liquefaction system were better understood, it might be possible to improve polyol quality.

Condensation reactions like i) and ii) in Figure 5.1, in which small molecular weight alcohols are involved, can improve the solubility of typically high molecular weight, insoluble, bark-biopolymers. This is essentially the role of the polyhydric alcohol solvent, to act as a reactive medium. However, bark-biopolymers can also undergo condensation reactions amongst themselves, resulting in highly insoluble compounds that form a residue. Therefore if the role of the polyhydric alcohol solvent on condensation reactions can be better understood, the liquefaction yield and the quality of the polyols can be improved.

It has been shown previously in the literature how the type of biomass[53] or species of bark, [119, 50] acid type and acid content, [45, 59] temperature, [58, 117] biomass-solvent ratio, [108] and glycerol content[58] impact liquefaction yield. However, few papers have discussed the role of the polyhydric alcohol structure. The most commonly used polyhydric alcohol solvent is a blend of PEG-400 and glycerol for polyurethane polyols. The very low equivalent weight of glycerol produces a reaction environment very rich in polar hydroxyl groups able to partake in the glycoysis of the bark compounds. Although the liquefaction yield is high, this presents two main issues. Firstly, the high composition of primary
Figure 5.1: The condensation reactions involving hydroxyl rich bark-biopolymers and the polyhydric alcohol solvent

i) Primary alcohols can undergo nucleophilic substitution with other alcohols to form ether linkages

\[
\begin{align*}
R_1\text{OH} & \quad \xrightarrow{H^+} \quad R_1\text{OH}_3 \quad \xrightarrow{H_2O} \quad R_1\text{O}R_2 \quad \xrightarrow{H^+} \quad R_1\text{OR}_2 \nend{align*}
\]

ii) Secondary alcohols and phenolics can undergo electrophilic aromatic substitution (Friedel-Crafts Alkylation)

\[
\begin{align*}
R\text{OH} & \quad \xrightarrow{H^+} \quad R\text{OH}_3 \quad \xrightarrow{-H_2O} \quad R\quad \xrightarrow{+} \quad \begin{array}{c}
\text{Ar} \\
\text{OMe}
\end{array} \quad \xrightarrow{-H_2O} \quad R\text{ArOMe}
\end{align*}
\]

iii) Alcohols with carboxylic acids go through nucleophilic acyl substitution (Fischer Esterification)

\[
\begin{align*}
R_1\text{COOH} & \quad \xrightarrow{H^+} \quad R_1\text{COOH}_3 \quad \xrightarrow{-H_2O} \quad R_1\text{CO}R_2 \quad \xrightarrow{-H_2O} \quad R_1\text{CO}R_2
\end{align*}
\]
alcohols produces a polyol that has a very short pot-life and foams rather violently.\textsuperscript{[118]} Secondly, the low equivalent weight, especially of glycerol, results in a highly friable foam. In contrast industry polyols are often composed of secondary alcohols and are triols with larger equivalent weights. In a study by Krzan et al. employing microwave liquefaction, it is shown that shorter molecular weight glycols like ethylene glycol and propylene glycol achieve higher liquefaction yields than their larger molecular weight counterparts, diethylene glycol and dipropylene glycol.\textsuperscript{[120]} This identifies molecular weight of the polyhydric alcohol as a factor; however no studies have investigated the impact of alcohol type or functionality.

Another aspect related to solvent selection that can improve liquefaction behaviour is the use of an organic co-solvent. This is advantageous for the following reasons. Firstly, organic solvents offer the possibility to tune the liquefaction to be more selective for a certain types of compound to extract. Hansen et al. demonstrated that solvents with a similar solubility parameter to the biomass component will improve solubility and extraction, therefore a lignin fragment will prefer hydrophobic solvents.\textsuperscript{[121]} Secondly, the solvation of reactive groups or radicals can also slow down or prevent unwanted side-reactions like charring or precipitation due to extensive recondensation reactions.\textsuperscript{[101]} Lastly, solvents can alter the reaction kinetics through improved acid dissociation of the acid catalyst. For example, carboxylic acids in water with a relative permittivity ($\epsilon_r$) of 78.3 have a $K_a$ value 106 times greater than if they were dissolved in ethanol ($\epsilon_r = 24.6$).\textsuperscript{[122]}

It has been shown that strongly polar solvents like amides, through ionic bonding, can swell biomass to such an extent that covalent bonds are ruptured and thereby improve accessibility.\textsuperscript{[121]} Unfortunately, selecting a solvent based on polarity is complex because many measures of polarity (dielectric constants, dipole moments, index of refraction; empirical polarity measurements) are required to be fed into solvent models like the linear free energy relationship (LSER) to develop a predictive model.\textsuperscript{[123]} Furthermore, some of these polarity measurements are temperature dependent, so the conditions of the liquefaction at 130 °C would be too extreme of an extrapolation. Therefore, in this work a variety of solvent polarity parameters were analyzed to see how well they correlate with liquefaction yield. This would aid in identifying which solvent parameters under the conditions of a liquefaction reaction are most relevant and can provide a guideline for future studies. The use of a co-solvent during liquefaction has been employed previously, but these attempts often used low-boiling solvents\textsuperscript{[48]} or simple alcohols like octanol.\textsuperscript{[124]}

The goals of this study are related to understanding how solvents impact the liquefaction behaviour and polyol properties of liquefied bark. Firstly, liquefaction yield will be studied with respect to the polyhydric alcohol structure (functionality, equivalent weight, and hydroxyl type), and co-solvent polarity. A series of liquefactions will be performed using different polyhydric alcohols and xylene as the co-solvent. Another series of liquefaction experiments will be done with PEG-400 as the polyhydric alcohol and the co-solvent will be varied. The residues from the liquefactions will then be characterized to determine how a solvent impacts residue composition and to better understand which factors governed the formation of insoluble residues (condensation products). Lastly, the polyols will be characterized by proton NMR to assess the degradation of sugars and the inclusion of aromatic compounds.
5.2 Results and Discussion

The effect of polyhydric alcohol structure on liquefaction yield

By varying the polyhydric alcohol and using xylene as the co-solvent the effect of the polyhydric alcohol functionality, equivalent weight, and alcohol type were discussed with regard to their effect on the liquefaction yield. The structure and naming convention used is detailed in Table 5.1. From a subset of the experiments, excluding polyhydric alcohols with extreme equivalent weights, it can be seen from Figure 5.2a that functionality does not have a significant impact on the liquefaction yield. It was expected that higher functionality polyhydric alcohols would have led to high molecular weight compounds that became insoluble and formed a residue; however this was not the case.

The next comparison examined the role of equivalent weight. Only glycol-based polyhydric alcohols were included in the data subset, and subdivided by type of alcohol. It is evident from Figure 5.2b that there was a negative correlation between equivalent weight and liquefaction yield. The Pearson’s correlation coefficient ($R_p$) for primary alcohols was -0.77 and for secondary alcohols was -0.64. This indicated that if shorter chain molecular weight polyhydric alcohols were used the yield can be increased, and that this effect was stronger with primary alcohols. By reducing equivalent weight the polyhydric alcohol solvent was more protic in nature, and thereby increased the ability to hydrogen bond and disrupted the lignocellulosic matrix. Furthermore, smaller molecular weight polyhydric alcohols have a lower molar volume (molecular mass / density) that was beneficial for achieving greater penetration and accessibility.

Finally, in order to understand the role of the hydroxyl type, all of the polyhydric alcohols were contrasted in Figure 5.2c with regard to their effect on liquefaction yield. Secondary hydroxyls achieved a consistent yield (average = 27.1 ± 4.1). However, polyols with primary hydroxyls showed a greater variation (average = 37.3 ± 32.5). This result reaffirmed the idea that as the equivalent weight was decreased for primary hydroxyls the yield can be improved. Since this effect was not observed for secondary hydroxyls, their mode of liquefaction might differ from that of primary hydroxyls and will be discussed in the following sections.

To summarize, these results revealed that low equivalent weight polyhydric alcohols with primary hydroxyl groups tended to have the highest yields, when other factors were kept constant. Also, since functionality did not seem to impact the liquefaction yield, this meant that liquefactions can be done in triols successfully. As a result, polyols could be designed to be more consistent with the typical glycerol-based triols or sucrose-based polyols used in rigid foam formulations.
Figure 5.2: The effect of a) functionality, b) equivalent weight, and c) hydroxyl type on the liquefaction yield using various polyhydric alcohols.
Table 5.1: Polyhydric alcohols and their structural characteristics

<table>
<thead>
<tr>
<th>polyhydric alcohol I.D.</th>
<th>chemical</th>
<th>molecular weight (Da)</th>
<th>functionality</th>
<th>liquefaction yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-2-75</td>
<td>Triethylene glycol</td>
<td>150</td>
<td>2</td>
<td>73.8</td>
</tr>
<tr>
<td>S-2-96</td>
<td>Tripropylene glycol</td>
<td>192</td>
<td>2</td>
<td>31.8</td>
</tr>
<tr>
<td>P-2-200</td>
<td>PEG-400</td>
<td>400</td>
<td>2</td>
<td>26.9</td>
</tr>
<tr>
<td>S-2-213</td>
<td>PPG-425</td>
<td>425</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>P-2-1025</td>
<td>PEG-2050</td>
<td>2050</td>
<td>2</td>
<td>11.3</td>
</tr>
<tr>
<td>S-3-86</td>
<td>Jeffol® G30-650</td>
<td>260</td>
<td>3</td>
<td>28.4</td>
</tr>
<tr>
<td>S-3-336</td>
<td>Jeffol® FX-31-167</td>
<td>1008</td>
<td>3</td>
<td>22.3</td>
</tr>
<tr>
<td>P-3-330</td>
<td>Jeffol® FE-12-60</td>
<td>990</td>
<td>3</td>
<td>17</td>
</tr>
<tr>
<td>S-4.4-157</td>
<td>Jeffol® SD-361</td>
<td>690</td>
<td>4.4</td>
<td>29.6</td>
</tr>
</tbody>
</table>

*a naming convention: alcohol type (primary-P; secondary-S)-functionality-equivalent weight*
Chapter 5. The effect of liquefaction solvents on the properties of bark-based polyols

The effect of an organic co-solvent on liquefaction yield

To examine the role of a cosolvent, the polyhydric alcohol used was PEG-400, while the co-solvent was varied and the liquefaction yield was measured. Their effect on yield can be seen in Table 5.2. It can be observed that ketonic solvents showed the greatest promise for increasing the liquefaction yield. To understand why this trend was observed, some of the commonly used measures of solvent polarity were correlated with liquefaction yield in Table 5.2. Both the index of refraction and the dielectric constant correlated poorly with yield. These measures are both related to the polarizability of the solvent. This result may be explained by the fact that as temperature increased the increase in kinetic energy of the solvent molecules randomized their orientations and thus reduced their dielectric constant. Furthermore, the poor correlation with parameters related to polarizability implied that the role of induced dipole-dipole interactions was minimal. The dipole moment and $E_N^T$ correlated well, which meant that the ability of the solvent to have charge separated and to engage in solvation plays a role in improving liquefaction.

The solvent polarity measurements that correlated best with liquefaction yield were the boiling point and the Hansen solubility parameter for hydrogen bonding ($\delta_h$). The boiling point represents how strongly a solvent molecule interacts with its solvent neighbours, so it can be a simple measure of polarity. However, since the liquefaction was done at 130 °C, using a higher boiling solvent may allow the reaction to occur at higher temperature if the reaction temperature was not controlled accurately. The strong correlation with $\delta_h$ was likely due to the fact that only the ketonic solvents AA and CH (data was not available for 2,4-dimethyl pentanone, DMP) have high values for $\delta_h$ (10.7, 11 MPa$^{1/2}$), while a solvent like xylene had a value of 2 MPa$^{1/2}$.[125] Although they are aprotic solvents, they have highly negatively charged carbonyls, and therefore are excellent proton acceptors / electron donors. The ability of a ketone’s carbonyl to donate electron density to a carbocation may have played a role in the prevention of condensation reactions.

The condensation reaction ii) shown in Figure 5.1 illustrates how a carbocation is attracted to the electron rich carbons in an arene.[126] Ketonic solvents have highly polar carbonyl groups resulting in the oxygen of the carbonyl being electron rich. It is proposed that the ketone’s carbonyl interacted with the carbocation radical, hence blocking the radical from undergoing condensation with an arene biopolymer. The role of the ketonic solvents in blocking condensation was further discussed in the sections on composition and carbon content analysis of the residues.

Due to scarcity of solvent polarity data, especially under the conditions pertinent to a liquefaction reaction, there have been few attempts to improve liquefaction through solvent selection. Research on the conversion and dissolution of biomass using reactive solvents like carbonates[127] and greener solvents like ionic liquids is expanding.[128] This preliminary study showed that there are simple characteristics that can be used to screen these emerging solvents.
### Chapter 5. The effect of liquefaction solvents on the properties of bark-based polyols

#### Table 5.2: The correlation between solvent polarity measurements and liquefaction yield

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\eta$</th>
<th>$V_m$ (cm$^3$/mol)</th>
<th>$\epsilon_r$</th>
<th>$\mu$</th>
<th>$\delta_T$</th>
<th>$T_{bp}$ (°C)</th>
<th>$\delta_d$</th>
<th>$\delta_p$</th>
<th>$\delta_h$</th>
<th>$\rho_p$</th>
<th>$R_p$</th>
<th>P-value</th>
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</thead>
<tbody>
<tr>
<td>xylene</td>
<td>1.49</td>
<td>102</td>
<td>124</td>
<td>1.3</td>
<td>2.56</td>
<td>135</td>
<td>18</td>
<td>9.4</td>
<td>17.1</td>
<td>7.2</td>
<td>-0.19</td>
<td>0.94</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>1.52</td>
<td>103</td>
<td>124</td>
<td>1.3</td>
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<td>135</td>
<td>18</td>
<td>9.4</td>
<td>17.1</td>
<td>7.2</td>
<td>-0.19</td>
<td>0.94</td>
</tr>
<tr>
<td>acetylacetone</td>
<td>1.45</td>
<td>104</td>
<td>124</td>
<td>1.3</td>
<td>2.56</td>
<td>135</td>
<td>18</td>
<td>9.4</td>
<td>17.1</td>
<td>7.2</td>
<td>-0.19</td>
<td>0.94</td>
</tr>
<tr>
<td>cyclohexanone</td>
<td>1.45</td>
<td>104</td>
<td>124</td>
<td>1.3</td>
<td>2.56</td>
<td>135</td>
<td>18</td>
<td>9.4</td>
<td>17.1</td>
<td>7.2</td>
<td>-0.19</td>
<td>0.94</td>
</tr>
<tr>
<td>DMP</td>
<td>1.4</td>
<td>104</td>
<td>124</td>
<td>1.3</td>
<td>2.56</td>
<td>135</td>
<td>18</td>
<td>9.4</td>
<td>17.1</td>
<td>7.2</td>
<td>-0.19</td>
<td>0.94</td>
</tr>
<tr>
<td>DMF</td>
<td>1.4</td>
<td>104</td>
<td>124</td>
<td>1.3</td>
<td>2.56</td>
<td>135</td>
<td>18</td>
<td>9.4</td>
<td>17.1</td>
<td>7.2</td>
<td>-0.19</td>
<td>0.94</td>
</tr>
<tr>
<td>DMP - 2,4-dimethylpentanone, DMF - dimethylformamide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\eta$ - index of refraction, $V_m$ - molar volume, $\epsilon_r$ - relative permittivity, $\mu$ - dipole moment, $\delta_T$ - Hildebrand solubility parameter, $T_{bp}$ - boiling point, $\delta_d$, $\delta_p$, $\delta_h$ - Hansen solubility parameters for dispersion, polar, and hydrogen bonding interactions. $R_p$ is the Pearson’s correlation coefficient.

All data was accrued from a mix of the following sources [122, 125, 129, 130], but the data was mostly sourced as follows: $\epsilon_r$ [129] — $V_m$ [130] — $\mu$, $\delta_T$, $T_{bp}$, $\delta_d$, $\delta_p$, $\delta_h$ [125].
The effect of solvents on the residue composition

Residue analysis plays an integral role in characterizing a polyol made from biomass, especially since a polyol is difficult to characterize directly. Therefore by characterizing the residues, one can infer what biopolymers were liquefied and converted into a polyol. The bark residue was characterized based upon the amount of extractives, AISL (acid insoluble lignin), and holocellulose. The effect of variation of the polyhydric alcohol solvent and of the cosolvent on composition is found in Figure 5.3 and Figure 5.4, respectively.

The first observation was that aside from P-2-75, all the other samples showed increased AISL content above that of the initial bark. This result was likely due to various biopolymers that underwent condensation reactions that lead to insoluble precipitates that resembled the characteristics of acid-insoluble lignin. This result was also observed in our previous work where a higher liquefaction temperature promoted condensation reactions and resulted in an increase in the AISL content.[117] Although the most likely culprit is the phenolic groups in the extractive compounds, this cannot be the sole contributor to the AISL fraction. This was evident from sample P-2-1050 where an AISL content of 61 % was observed. This implied that in addition to the extractive compounds, compounds belonging to the holocellulose fraction are also undergoing chemical modification and rearrangement to form precipitates. Pentoses from hemicellulose are known to form furfuryl alcohol and thereafter form insoluble humic structures.[131] This is corroborated by work done on the dilute acid-hydrolysis of softwood that shows the AISL content increases by 135 % and described this as a pseudo-lignin. This was ascribed to the condensation products of carbohydrates and extractives.[131]

From comparison of all the polyhydric alcohols, it appeared that highly polar polyhydric alcohols were the most effective at the prevention of AISL / pseudo-lignin formation. Large molecular weight polyhydric alcohols like P-2-1050 and S-2-1000 were essentially non-polar since their hydroxyl end groups were diluted by the long molecular weight chain. As a result, they had the highest AISL values at 61 % and 45 % respectively. Secondary alcohols are known to be less polar than primary alcohols,[129] and as a result the S-2-96 (39 %) residue had a higher AISL content than P-2-75 (14 %). The mechanism of the polyhydric alcohols preventing AISL formation can be explained through the formation of a protective solvation shell. Short chain primary alcohol solvents produced a highly polar protic environment. This enabled the diol to act as a shield that hindered reactive carbocations from undergoing condensation reactions. Primary alcohols can undergo a (S₂) nucleophilic substitution with other alcohols. Therefore the primary alcohol solvation shell blocked condensation with other bark biopolymers that would lead to residue formation, and instead promoted the grafting of the diol through etherification (Figure 5.1, reaction i).

Previous attempts to limit AISL formation focused on the addition of simple phenolics to quench reactive groups. Work done by Sealy et al.[29] and Wayman et al.[36] observed that the addition of simple phenolics like phloroglucinol and resorcinol, respectively, could curtail the formation of insoluble residues. This is because their high concentration and nucleophilicity enables them to condense on reactive carbocations, preventing those reactive species from undergoing condensation reactions with other high molecular weight biopolymers. The addition of phenolic groups into a polyol is undesirable since urethane linkages made from phenolic alcohols are not thermally stable.[24]

After studying the effect of the polyhydric alcohol solvent, the use of an organic cosolvent was studied. P-2-200 (PEG-400) was used as a polyhydric alcohol and the organic cosolvent was varied. The effect on the residue composition can be seen in Figure 5.4. The primary observation was that the use of xylene,
chlorobenzene (CB), and 2,4-dimethylpentanone (DMP) resulted in an increase in the AISL / pseudo-lignin content. This implied that these solvents were ineffective at preventing condensation reactions. Although DMP is a ketonic solvent, the presence of so many electron donating methyl groups in its structure greatly reduced the polarity of the solvent. The highly charge separated ketonic solvents like acetyl acetone (AA) and cyclohexanone (CH) had the lowest amount of acid-insoluble lignin / pseudo-lignin (condensation products). This supported the claim that AA and CH play a role in preventing condensation reactions.

The final observation was that of the 58 % holocellulose content of the bark, roughly two thirds of that remains as a residue. This may be due to the large fraction of hemicelluloses that were easily broken down, while the cellulose was resistant to the treatment. Lodgepole pine bark has a sugar content of glucose (50 %), galactose (7 %), mannose (6 %), arabinose (26 %), and xylose (8 %).[132] With such a high percentage of hemicelluloses and the likelihood that some of that glucose is amorphous cellulose, it would be expected that more of the holocellulose would be liquefied. The likely explanation was that since these sugars exist in a hierarchical structure, their accessibility and conversion takes extended time. This was also consistent with the fact that all the residues had some extractives compounds remaining. Liquefaction for one hour was unable to extract them from the cell walls, but a 6 hour soxhlet extraction succeeded. A finer mesh size for grinding the bark may be used to improve the yield; however, longer reaction times[64] and higher temperature[117] should be avoided since they increase the amount of sugar degradation.
Figure 5.4: The amount of bark liquefied into a polyol and the composition of the unliquefied residue depending on the cosolvent used. CB - chlorobenzene, AA - acetyl acetone, CH - cyclohexanone, DMP - 2,4-dimethylpentanone, DMF - dimethylformamide. AISL - Acid Insoluble Lignin, Holo - Holocellulose (cellulose and hemicelluloses)
Assessing the extent of condensation reactions in the residue

Elemental analysis is commonly used to verify the chemical structure of purified compounds; however it can also be used to assess the extent of chemical reactions. Heitz et al. conducted a similar analysis using a ratio of the carbon / oxygen content to examine the extent of condensation reactions.\[101] In Figure 5.1 a series of condensation reactions are depicted. These reactions released oxygen in the form of water and consequently the carbon content increases. Condensation reactions could also increase molecular weight and thereby reduce solubility, resulting in insoluble precipitates. Therefore, by analyzing the residues with respect to their carbon content, an insight into the extent of condensation reactions can be made.

The effect of different organic solvents and of different polyhydric alcohol solvents on the carbon content can be seen in Table 5.3. The first observable trend was that polar solvents seemed to reduce the carbon ratio, which implied that polar solvents prevented condensation reactions from occurring and thereby prevented the formation of insoluble residues. The residue from liquefaction in xylene, a non-polar solvent, had nearly the same carbon ratio as that of the initial bark. Chlorobenzene, which was slightly more polar, had a lower carbon ratio, and more polar solvents had even lower carbon ratio values. Both AA and CH have the lowest carbon content values and supported the claim that these solvents played a role in preventing condensation reactions through their dipole interactions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C % / C_{Bark} %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bark</td>
<td>1</td>
</tr>
<tr>
<td>P-2-2-200</td>
<td>1.03</td>
</tr>
<tr>
<td>S-2-213</td>
<td>1.02</td>
</tr>
<tr>
<td>P-2-1025</td>
<td>1.13</td>
</tr>
<tr>
<td>P-2-75</td>
<td>0.99</td>
</tr>
<tr>
<td>P-3-330</td>
<td>1.05</td>
</tr>
<tr>
<td>xylene</td>
<td>1.03</td>
</tr>
<tr>
<td>chloro benzene</td>
<td>0.96</td>
</tr>
<tr>
<td>acetyl acetone</td>
<td>0.78</td>
</tr>
<tr>
<td>cyclohexanone</td>
<td>0.71</td>
</tr>
<tr>
<td>DMP</td>
<td>0.96</td>
</tr>
<tr>
<td>DMF</td>
<td>0.87</td>
</tr>
</tbody>
</table>

With regard to the polyhydric alcohols, all the polyhydric alcohols that have low equivalent weights behaved more like a protic, polar solvent and have roughly a carbon ratio of one, and thus showed a protective effect. Sample P-2-1025 had the highest equivalent weight, which gave it the character of a very dilute protic solvent, and therefore it acted non-polar and had the highest carbon ratio. The solvation of bark bio-polymers by highly polar solvent molecules could explain why the formation of insoluble condensation products was reduced.

To summarize, low equivalent weight polyhydric alcohols and polar organic solvents showed a protective effect against condensation. The first may be attributed to the formation of a solvation shell through hydrogen bonding, while the latter could involve dipole interactions. These interactions of
the biopolymers hydroxyl group with either the polyhydric alcohol solvent or a cosolvent may alter its reactivity and thereby hinder condensation reactions.

**The effect of polyhydric alcohols on polyol viscosity and hydroxyl value**

Viscosity is a key characteristic of a polyol since it is intrinsically linked to molecular weight and is a determinant of how well a polyol mixes with an isocyanate and bubble growth kinetics. The viscosity of the polyols had a strong correlation ($R_p = 0.91$, $P = 0.03$) with the functionality of the polyhydric alcohol solvent used during the liquefaction. In Figure 5.5 only polyols with medium equivalent weight were shown for a simpler comparison, and revealed a clear trend that as the solvents functionality increased, the liquefied product had a higher viscosity. This is simply explained since a greater amount of functional groups would have lead to a greater amount of grafting and thus increased the molecular weight, and therefore the viscosity. Another observation was that the methyl group in the PPG chains plays a role in preventing intermolecular interactions. This was demonstrated by the fact that S-2-1000 had a low viscosity of 757 cP while P-2-1050 had solidified.

![Figure 5.5: The effect of functionality and hydroxyl type on polyol viscosity](image)

The hydroxyl value is a critical characteristic of a polyol since it represents the number of reactive hydroxyl groups. Polyols for rigid foam formulations generally have an hydroxyl value (OHV) from 300 - 600 mgKOH/g.[68] From Table 5.4 it can be seen that liquefactions done in polyhydric alcohols with lower equivalent weights were able to meet this criteria, while the higher equivalent weight samples would be better suited for flexible foam formulations. There also appeared to be a decrease in the OHV when using polyhydric alcohols with secondary alcohols. This suggested that when secondary alcohols are present more condensation reactions occur, resulting in a lower OHV. This was most evident with S-3-336 and P-3-330, where their equivalent weights were nearly the same and yet their OHVs were substantially different, 138 versus 200 mgKOH/g. However, a small part of this difference can also be attributed to the methyl group of the secondary alcohol that results in a higher equivalent weight, and therefore lower OHV. A chi-squared test of all the samples yielded a $P$ value of 0.25, which does not meet the 95 % confidence interval typically used; however a confidence of 75 % would still seem to imply a trend. This was an important finding since it linked the extent of condensation reactions to the type of alcohol in the polyhydric alcohol solvent used.
Table 5.4: The change in polyol characteristics through variation of the polyhydric alcohol liquefying solvent

<table>
<thead>
<tr>
<th>polyhydric alcohol</th>
<th>bark fraction (%)</th>
<th>hydroxyl value (mgKOH/g)</th>
<th>viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-2-75</td>
<td>27</td>
<td>585 ± 4</td>
<td>2360</td>
</tr>
<tr>
<td>S-2-96</td>
<td>13.7</td>
<td>537 ± 5</td>
<td>390</td>
</tr>
<tr>
<td>P-2-200</td>
<td>11.9</td>
<td>315 ± 6</td>
<td>780</td>
</tr>
<tr>
<td>S-2-213</td>
<td>11.1</td>
<td>254 ± 17</td>
<td>170</td>
</tr>
<tr>
<td>P-2-1025 b</td>
<td>5.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S-2-1000</td>
<td>10.9</td>
<td>132 ± 14</td>
<td>757</td>
</tr>
<tr>
<td>S-3-86</td>
<td>12.4</td>
<td>573 ± 36</td>
<td>9770</td>
</tr>
<tr>
<td>S-3-336</td>
<td>10</td>
<td>138 ± 9</td>
<td>630</td>
</tr>
<tr>
<td>P-3-330</td>
<td>7.8</td>
<td>200 ± 6</td>
<td>1550</td>
</tr>
<tr>
<td>S-4.4-157</td>
<td>12.9</td>
<td>254 ± 2</td>
<td>2900</td>
</tr>
</tbody>
</table>

a naming convention: alcohol type (primary-P, secondary-S)functionality-equivalent weight

b Sample P-2-1050 could not be analyzed because it was a solid sample
c determined from the liquefaction yield and the mass of glycerol and polyhydric alcohol solvent used

Assessment of the aromatic content and sugar degradation in the polyol

Determination of the viscosity and hydroxyl value are key parameters for the practical use of a polyol. However, in order to understand a polyols structure, especially one derived from liquefied natural materials, a greater depth of analysis is needed. Proton NMR is highly practical since its high sensitivity enables quantification of structural features through the integration of certain regions. This was shown in Figure 5.6 where the proton spectrum of P-2-200 was magnified to depict the regions related to the degradation of sugars and aromatic compounds.

The degradation of high functionality sugars into low molecular weight, low functionality degradation products have negative implications for the polyol properties, and resultant foam properties. The protons associated with formic and levulinic acids were integrated to assess the amount of degradation, and the values were made relative to the degradation observed from the P-2-200 sample (PEG-400, the standard polyhydric alcohol solvent). From Table 5.5 it can be seen that there was a significant difference between the amount of degradation and the type of polyhydric alcohol used during liquefaction. This trend was more evident in the box plot in Figure 5.7, where both the mean amount of degradation and the range for secondary alcohols (1.34, 1–1.6) was higher than primary alcohols (0.83, 0.6–1). This was consistent with the above findings from the residue analysis that showed that primary alcohols were more effective at preventing AISL / pseudo-lignin formation. It was proposed that the greater polarity of primary alcohols enabled hydrogen bonding and the formation of a protective solvation shell that prevented degradation reactions from occurring. The greatest amount of degradation was observed for the sample S-4.4-157. Since the S-4.4-157 was a blend of propoxylated sucrose and diethylene glycol it would be expected that those sugars might have degraded under the liquefaction conditions and contributed to the amount of degradation products.

The presence of aromatic structures in the polyol indicated that the conditions used were favourable for preserving their structures unscathed. From Table 5.5 the aromatic content may have been influenced by the alcohol type. P-2-200 and S-2-213 have similar functionality and equivalent weight, and yet the primary alcohol has a higher aromatic content. P-2-75 also had a higher aromatic content than S-
Figure 5.6: The H-NMR Spectra of bark polyol using P-2-200 as a polyhydric alcohol solvent. Integration areas used for determining the amount of degradation (L_5-levulinic acid and F_1-formic acid) and the aromatic content are shown.

Figure 5.7: As determined by H-NMR, the relative amount of sugar degradation products based on the type of hydroxyl in the polyhydric alcohol solvent. All samples were made relative to P-2-200 as the basis of comparison.
2-96. This observation may have been biased since a higher liquefaction yield would have inherently incorporated a greater fraction of aromatic groups. P-2-75 had the highest liquefaction yield and also had the highest aromatic content.

Table 5.5: H-NMR was used to assess the relative amount of degradation and aromatics content of the bark-based polyols

<table>
<thead>
<tr>
<th>polyhydric alcohol b</th>
<th>relative degradation a</th>
<th>relative aromatics a</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-2-75</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>S-2-96</td>
<td>1</td>
<td>0.7</td>
</tr>
<tr>
<td>P-2-200</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>S-2-213</td>
<td>1.6</td>
<td>0.7</td>
</tr>
<tr>
<td>S-2-1000</td>
<td>1.1</td>
<td>0.4</td>
</tr>
<tr>
<td>S-3-87</td>
<td>1.4</td>
<td>0.9</td>
</tr>
<tr>
<td>P-3-330</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>S-3-336</td>
<td>1.6</td>
<td>0.9</td>
</tr>
<tr>
<td>S-4.4-157</td>
<td>2.3</td>
<td>0.9</td>
</tr>
</tbody>
</table>

a The determination of the relative amounts of degradation and aromatic content was based upon a comparison to the PEG-400 sample (P-2-200) and the methodology used was described in the experimental section

b naming convention: alcohol type (primary-P, secondary-S)functionality-equivalent weight

5.3 Conclusions

The liquefaction of bark in polyhydric alcohols with varying structural characteristics and with solvents of varying polarity and structure have produced insights into the effectiveness of liquefaction, the composition of the unliquefied residues, and the solvent factors that influenced the condensation reactions that resulted in AISL / pseudo-lignin formation.

Liquefaction yield was found to increase with decreasing equivalent weight. Polyhydric alcohols with secondary hydroxyls had a consistent yield, while those with primary hydroxyls showed a stronger dependence on equivalent weight. This showed that the highly polar hydroxyls (primary) and short chains created a highly protic solvent that improved conversion. Regarding organic cosolvents, ketonic solvents showed the greatest increase in the liquefaction yield. When liquefaction yield was correlated with various solvent polarity measurements, the highest correlation was achieved with the Hansen solubility parameter for hydrogen bonding ($\delta_h$). The ability of the ketone’s carbonyl to behave as a proton acceptor / electron donator may have facilitated interactions with carbocations that effectively blocked condensation reactions with biopolymer arenes. The composition and carbon content analysis of the residues also suggested that ketonic solvents like acetyl acetone and cyclohexanone may have played a role in preventing condensation reactions.

Analysis of the composition of the liquefaction residues showed that short chain primary hydroxyl alcohols were most effective at preventing AISL / pseudo-lignin formation. It was proposed that under these conditions the solvent was highly protic and the ability to hydrogen bond created a protective
solvation shell that inhibited condensation reactions with other biopolymers. Finally, elemental analysis of the residues was used to identify the extent of condensation reactions, since the loss of water will have increased the carbon content. It was found that polar organic solvents and low equivalent weight polyhydric alcohols had a lower carbon ratio, and therefore less condensation reactions occurred.

Determination of the hydroxyl value of the polyols also proved insightful. A slight trend was observed of lower OHV values for secondary polyhydric alcohol compared to primary. This indicated that condensation reactions may occur to a greater extent when secondary alcohols are present. This is consistent with the H-NMR analysis that showed a greater amount of sugar degradation products when secondary alcohols were used. These results have shown that the selection of polyhydric alcohols and organic cosolvents have had a significant impact on the liquefaction yield and the polyol characteristics. The effect of the polyhydric alcohol solvent was especially important since it remains as the dominant constituent of the bark-based polyols and will largely dictate the PUF behavior. With a better understanding of how solvent impacts liquefaction it will be possible to have greater control over the properties of the polyol and improve the viability of bark-based PUFs.
Chapter 6

The effect of liquefaction temperature on foam characteristics

The following work has been adapted from the Journal of Applied Polymer Science:


6.1 Introduction

Chapter 4 showed that a liquefaction at 160 °C produced a large amount of condensation products that would reduce functionality, had a high viscosity, and had a large amount of sugar degradation products. Therefore, polyols were synthesized through solvent liquefaction in a blend of polyethylene glycol (PEG-400) / glycerol (95:5, %w/w) solvent at only temperatures of 90 and 130 °C. These bark polyols featured a hydroxyl value, hydroxyl type, and viscosity consistent with typical industrial polyols for making rigid PUFs.

What remains unknown is how the presence of liquefied bark compounds with unknown functionality and a broad molecular weight profile will impact foam characteristics like the foaming kinetics, the morphology, and the polymeric nature of the polyurethane polymer. These polyols were used to produce the bark-based foams B90 and B130. These were contrasted to two control foams, PEG-G and PPG-G, made from a blend with polyethylene glycol 400 / polypropylene glycol 425 and glycerol (95:5, %w/w).

The goals of this study are two-fold. Firstly, by comparing the bark-based foams to controls the effect of the inclusion of liquefied bark bio-polymers on foam properties can be examined. Secondly, the effect of the liquefaction temperature on properties of bark-based PUFs can be studied. Understanding the effect of bark bio-polymers and the liquefaction conditions on foam properties is essential to determining the applicability of liquefaction as a process for the conversion of bark into a polyol.
6.2 Results and Discussion

Foaming kinetics

The kinetics of polyurethane reactions have been traditionally studied by attenuated total reflectance infrared spectroscopy (ATR-FTIR),[86, 133] dynamic scanning calorimetry (DSC),[134] and by novel methods looking at changes in resistivity.[135] However, the kinetics of the polyurethane foams made from liquefied polyols have not been examined to the same extent. In this work, analysis of the rate of foaming and the temperature profile were used to facilitate inferences about the reactivity of the polyols, morphology, and density. The latter two are both key determinants of mechanical properties and therefore illustrate the need for understanding the foaming kinetics.

The graph in Figure 6.1a shows that the PEG-glycerol based foam (PEG-G) and the bark-based B90 and B130 exhibited rapid increases in temperature upon initiation of the foaming reaction. These foams are all based upon a PEG-glycerol structure and therefore have a very high fraction of primary alcohols. Since primary alcohols react more exothermically than secondary alcohols the PEG-based samples resulted in higher temperatures and a faster foaming rate as shown in Table 6.1. In contrast, the PPG-G foam predominantly consisted of secondary alcohols that resulted in less heat generation. This slower curing profile is ideal since it allows greater amounts of time to ensure proper mixing, and will promote a more controlled foaming that is more isotropic. The heat evolved and the reaction temperature were not managed or controlled. The reaction could be done in a temperature controlled environment to negate these observed differences in reaction temperature. Otherwise, if the foaming rates are not similar then the mixing of the isocyanate with the polyol may need optimization. For example, if a foam reacts faster than expected, the pre-polymer mixture may be sheared by the mixer as it is polymerizing, resulting in possibly damaged cells.

The change in height of foams provides insight into the dimensional stability of the foaming polymer. From Figure 6.1b the PPG-G polyol has a near linear increase that smoothly transitions into a plateau. The other control foam, PEG-G behaves similarly initially, but after it reaches its maximum height it proceeds to shrink. This shrinkage may be due to its higher reaction temperature that resulted in a greater pressure drop as the CO\textsubscript{2} cools. The bark-foams interestingly exhibited a small amount of shrinkage and then remained constant. One possible explanation was that the low amount of closed-cell content of the bark foams at roughly 1-3% as shown in Table 6.3 enabled the gas to equilibrate. In contrast, the PEG-G foam with its higher closed-cell contents of 64 % is more susceptible to the low pressure vacuum created by CO\textsubscript{2} cooling. Regarding morphology, rapid foaming will tend to exhibit anisotropic characteristics as the rise direction is elongated. This can be observed in the optical microscopy images in Figure 6.5 d,f,h in the rise direction corresponding to PEG-G, B90, and B130 foams, whereas PPG-G did not show any elongation. The density of foams may also have been impacted by the foaming kinetics. The PEG-G foam had the highest reaction temperature, and therefore the gas probably exhibited the greatest pressure drop and thus may explain the shrinkage observed in the PEG-G foam and the higher density value observed for that foam. Since the polymerization was done in a cup it was possible to measure the rate at which the foam expanded in the vertical direction, but the foaming was unconstrained. Had the foaming been done in a sealed environment, it would have been possible to keep the foams at a fixed density. Furthermore, performing the foaming in a temperature controlled environment could allow for differences due to heat evolution during the reaction to be minimized.
Chapter 6. The effect of liquefaction temperature on foam characteristics

Figure 6.1: Analysis of the foaming kinetics a) shows the change in temperature during the foaming reaction and b) shows the rate of expansion to reach the maximum height.

Table 6.1: Parameters used to assess the foaming kinetics

<table>
<thead>
<tr>
<th></th>
<th>Maximum Temperature (°C)</th>
<th>Time of Maximum Temperature (s)</th>
<th>Temperature Rate of Change dT/dt (°C/min)$^a$</th>
<th>Time to Maximum Height (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPG-G</td>
<td>74</td>
<td>210</td>
<td>21</td>
<td>88</td>
</tr>
<tr>
<td>PEG-G</td>
<td>97</td>
<td>125</td>
<td>47</td>
<td>25</td>
</tr>
<tr>
<td>B90</td>
<td>90</td>
<td>142</td>
<td>36</td>
<td>45</td>
</tr>
<tr>
<td>B130</td>
<td>79</td>
<td>119</td>
<td>39</td>
<td>28</td>
</tr>
</tbody>
</table>

$^a$ This value is the rate at which the foam reaches its maximum temperature.
Chapter 6. The effect of liquefaction temperature on foam characteristics

Chemical characteristics of the polyurethane

The polyurethane polymer was studied by analyzing its functional groups by attenuated total reflection spectroscopy (ATR) and the stability of its polymer network by thermogravimetric analysis (TGA). The cross-linking behaviour was studied indirectly via determination of the glass-transition temperature by dynamic mechanical rheometry, a solvent swelling test, and the soluble fraction.

TGA under an inert environment can provide insight into the composition through differences in the thermal stability of chemical bonds. The thermal decomposition of polyurethanes has been described as a combination of random-chain scission, chain-end unzipping, and cross-linking.[24] From the literature, the urethane (200 °C) and urea (250 °C) linkages are the first to break and depolymerize back into free isocyanate and the alcohol. This is followed by degradation of the polyether polyols, and finally isocyanate past 600 °C.[136]

It was expected for B130 to have the lowest residue amount, since it had the lowest hydroxyl value and correspondingly the lowest weight fraction of thermally stable aromatic rings from the MDI structure. Instead, both bark foams showed higher amounts of char formation than the control foams. One possible explanation may be that the large molecular weight and aromatic structure of bark extractives lend themselves to char formation more easily than a polyether polyol.

In the Derivative of TGA (DTGA) graphs in Figure 6.2b, it can be seen that B90 began to degrade earlier than the other foams at around 200 °C. This may be attributed to the decomposition of sugars from the P90 polyol.[137] After this initial degradation, the urethane linkage depolymerized to produce free isocyanate and polyol.[138] From the DTGA graphs PEG-based polyols degraded throughout the temperature range of 250-400 °C and resulted in large mass losses, with one large degradation maxima at 320 °C, followed by a significantly smaller peak at 400 °C. In contrast, PPG-G had degradation maxima at 285 °C and 365 °C. These two peaks indicated differences may exist in phase behaviour between the PPG-PUF and the PEG-based PUFs. Previous research has shown that in an inert environment PEG-based polyurethanes are more thermally stable due a mutual stabilizing effect caused by extensive amounts of inter-urethane hydrogen bonding between intermixed hard and soft segment phases.[139] In contrast, PPG prevents miscibility of the phases. Without a mutual stabilizing effect the PPG polyl degraded at lower temperatures than the PEG system.

Figure 6.2: a) TGA and b) differential-TGA of control foams FX and PG versus bark-based foams B90 and B130; both under nitrogen
Under an inert environment, these results showed that the PEG structure of the polyols produced more thermally stable PU polymers compared to a PPG-PUF. This has been described as a shielding effect due to mixed hard and soft segments. It can be seen that the inclusion of bark did not significantly impact the degradation behavior, other than increasing the amount of char formation visible in Figure 6.2a.

The polyurethane polymer structure was studied by analyzing its functional groups using attenuated total reflectance spectroscopy (ATR). The ATR spectra of the four foams are shown in Figure 6.3. All the foams have peaks that correspond to functionalities found in ureas and urethanes: a broad N-H peak at 3300 cm\(^{-1}\), C-H peak at 2900 cm\(^{-1}\), carbonyl peaks from 1650-1750 cm\(^{-1}\), an aromatic ring stretch at 1580-1615 cm\(^{-1}\), peaks from 1190-1130 cm\(^{-1}\) are characteristic of a C-N stretch of an aromatic secondary amine,[140] and the urethane linkage at approximately 1200 cm\(^{-1}\).[141] PPG-G, B90, and B130 show a peak for unreacted isocyanate at 2275 cm\(^{-1}\), despite a relatively low isocyanate index of 1.1. Using beer-lamberts law it is possible to use the isocyanate peak to determine the change in concentration over time. This would be of useful for determining if the curing of the isocyanate is affected by the variation in hydroxyl types present from biomass. Additionally, it could be used to assess if the polymer system underwent vitrification since the amount of isocyanate consumed would be higher if curing was incomplete. In addition to the formation of urea and urethane linkages, isocyanate can also undergo dimerization reactions to produce carboimides, as well as a trimerization reaction to produce an isocyanurate ring. Carboimides have a peak at 2140 cm\(^{-1}\) and can be observed as a small shoulder in B130, and small peaks in PPG-G and PEG-G. All four foams showed a peak at 1415 cm\(^{-1}\) that was indicative of an isocyanurate ring.[141] Isocyanurate rings increase the cross-linking density and are also stable at high temperatures. Catalysts were used to promote the gelling (urethane linkage) and blowing (urea linkage) reactions. However, these catalysts are also known to have some activity at promoting isocyanurate formation.[142] In summary, the ATR results showed that the bark polyols reacted with isocyanate, leaving only a small residual NCO peak, and produced a mixture of urea and urethane linkages, consistent with a typical PUF.

The cross-linking behaviour was studied indirectly via determination of the glass-transition temperature by dynamic mechanical rheometry, a solvent swelling test, and the soluble fraction. Determination of the glass transition temperature (\(T_g\)) provides insight into the observed mechanical properties through the effect of molecular weight, aromatic content, and cross-linking density on chain mobility. From the
plot of the storage modulus of the four foams in Figure 6.4 it was evident that PPG-G had the steepest decline in the storage modulus, whereas the PEG foams had a delayed onset of storage modulus decay. This indicated a difference in the phase morphology may have existed. PEG-based PUFs tend to have increased miscibility between hard and soft segments,[143] which could have delayed the decrease in storage modulus. Focusing on just the PEG-based foams (B90, B130, PEG-G), the storage modulus behaviour at room temperature for the bark foams was similar to PEG-G, but differed at elevated temperatures. B90 had its storage modulus decay the slowest, followed by the PEG-G foam, and lastly B130. These differences may be explained by a difference in the molecular weight between cross-links ($M_c$) with a small $M_c$ indicative of a very rigid polymer. B90 has a large fraction of low molecular weight compounds that could have greatly reduced the $M_c$, despite the fact that it had a similar hydroxyl value to PEG-G. B130 however had the lowest hydroxyl value of the three, and therefore its $M_c$ was expected to be the highest, and have the lowest storage modulus. Another observation was that only the PEG-G foam showed a clear rubbery plateau in its plot of storage modulus. This indicated a cohesive network with extensive curing. The high temperature of 97 °C observed in the foaming kinetics data in Table 6.1 could have prevented any vitrification from occurring. Therefore, reactive hydroxyl groups had enough thermal energy to find isocyanate groups ($T_{rx} > T_g$ of PUF) and by reacting increase the cross-link density. In contrast, the bark foams and PPG-G that evolved less heat during the reaction have not exhibited a rubbery plateau and therefore may not have cured completely or have a more fragmented network. Since the curing is an aspect of processing, it may be possible to do the reaction in a controlled heated environment to address this issue in future work. Therefore, it would appear that phase behaviour, polyol molecular weight, and curing temperature may all have had an impact on the thermo-mechanical properties of the PUFs.

The peak of the tan delta graph in Figure 6.4 was used to determine the glass transition temperature. All four foams have a glass transition temperature within the range of 145-160 °C. The PPG-G foam had the highest at 157 °C, while PEG-G (145 °C) and B130 (151 °C) were slightly lower. The B90 foam did not exhibit a clear peak, but rather a slope change that occurred at approximately 151 °C. The lack of a clear peak indicated that the B90 foam may have had a very broad range of molecular weight chains. The glass transition of B130 was within a few degrees of PEG-G, but interestingly the intensity of the tan delta peak was significantly less. Since tan delta is the ratio of the loss modulus to the storage modulus, a less intense tan delta peaks implied that the foam exhibited greater elastic behaviour and restricted viscous flow. It’s been shown previously in the literature that increased functionality results in less intense tan delta peaks and higher glass transition temperatures.[144] This result suggested that B130 has a high functionality.

The degree of swelling is a useful metric to indirectly assess the degree of cross-linking. As the cross-linked polymer network absorbs solvent its expansion is restricted by the network. Polymers that are lightly cross-linked will tend to absorb more solvent as the sample’s volume swells, while samples that are heavily cross-linked do not expand as much and therefore there is limited volume for solvent absorption. From Table 6.2 it can be seen that all the foams exhibited a similar extent of swelling. This was consistent with the aforementioned glass transition values that were within a narrow range, which implied that the foams had sufficient cross-linking to resist swelling. However, by assessing the soluble fraction as shown in Table 6.2 it can be seen that B130, and to a greater degree B90, have polymer chains that have not been fully incorporated into the PUF network compared to the control foams PPG-G and PEG-G. Since degraded bark components may have low functionality, or perhaps none at
Figure 6.4: Storage modulus / tan delta of control PUFs (PPG-G, PEG-G) and bark PUFs (B90, B130)
all, these can be leached easily from the PUF. It should be noted that B130 shows a lower degree of swelling and soluble fraction than B90. The P90 polyol used to make the B90-PUF was shown to have contained a large fraction of low-molecular weight compounds compared to the P130 polyol used to make B130.\[117\] These soluble fraction values were quite low with some contribution likely originating from leached catalyst and surfactant. Control samples contain the same amount of catalyst and surfactant, but may exhibit differences in solvent permeability that arose from the primarily open-celled bark foams as shown in Table 6.3.

The results of the polymer characteristics can be summarized by the following: The high fraction of low molecular weight compounds in B90 produced a high storage modulus value at elevated temperatures, possibly due to a short $M_c$. However, a higher liquefaction temperature produced a more uniform polyol, and the corresponding foam B130 exhibited a clear glass transition temperature that was more consistent with the control samples. By assessing the soluble fraction, B130 and to a greater extent B90, have polymer chains that have not been fully incorporated into the PUF network. Removal of these low-molecular weight compounds from both polyols may be one method to improve the characteristics of bark-based PUFs as these compounds appeared to hinder the formation of a cohesive polymer network.

| Table 6.2: Swelling and soluble fraction data of the control and bark-based PUFs |
|--------------------------------|----------------|----------------|----------------|----------------|
|                                | PPG-G          | PEG-G          | B90            | B130           |
| degree of swelling             | 1.23±0.00      | 1.10±0.01      | 1.44±0.06      | 1.22±0.03      |
| soluble fraction (%)           | 0.14±0.23      | 0.53±0.15      | 1.70±0.21      | 1.47±0.16      |

**Morphology of the PUFs**

The morphology of PUFs are known to correlate with many material properties, although thorough characterization of the morphology through microscopy is rarely done because it is often plagued by complexities associated with getting reproducible data and selection of appropriate methods.\[91\] Nonetheless, the optical micrographs in Figure 6.5 qualitatively showed that both controls (PPG-G, PEG-G) and B130 had the most uniform periodic cellular structure, whereas greater heterogeneity was observed for B90. All foams had some large pores indicating the coalescence of cells had occurred, but B90 appeared to have these defects at a greater frequency. Furthermore, the optical micrographs in Figure 6.5e-h show that the cellular structure was less defined in the bark foams, especially B90. Conversely, the cell structures of PPG-G and PEG-G in Figure 6a-d had sharper boundaries. This result implied that the bark polyols, especially the B90 polyol, had not formed a stable network quick enough to preserve a cell structure, but rather underwent Ostwald ripening.

Aside from microscopy, the morphology can also be probed through characterization of the closed-cell content. This is an important characteristic of cellular materials due to its influence on heat transfer and the cell membranes role in elastic stretching. It can be seen from Table 6.3 that both bark-based foams had low values for closed-cell content compared to the control foams. Since the curing profiles of the bark foams were intermediate to both controls this was likely not due to the kinetics of foaming. Also, the bark polyols had a higher viscosity, so it was expected for them to have thicker membranes. Therefore, the low values for the closed-cell content could have originated from low-functionality compounds in the bark polyols. These compounds could have ruptured membranes by plasticizing them and prevented a cohesive polymer network from being formed in the membrane, and thus resulted in greater amounts...
of polymer drainage from the film. Alternatively, compounds from the bark could have also acted as an anti-foaming agent by reducing surface tension.[145] Removal of low molecular weight compounds (likely with low functionality) may remedy the low amount of closed cells. Furthermore, optimization of the formulation, regarding the content and type of both surfactant and catalysts may help to improve the closed-cell content since the reactivity and the surface energy of bark polyols could differ from the controls.

Lastly, the foams were compared in the rise and transverse directions and it can be observed that the cells were stretched along the rise direction in all the foams, but B130 appeared to have been the least anisotropic foam with the least amount of elongation. Cell heterogeneity varied along the rise direction and as result this could have been an artifact associated with sample selection and foam preparation within a cup. The cause of anisotropy is generally due to the cells expanding in the least constrained direction, the rise direction. Had the reaction been done in a mould it would likely eliminate the observed anisotropy.
Figure 6.5: Optical micrographs of the foams a,b - PPG-G; c,d - PEG-G; e,f - B90; g,h - B130; horizontal/vertical scale bars represents a foam sample in the transverse/rise direction, respectively.
Mechanical Properties

To understand the compressive behaviour of PUFs it is important to begin with a discussion of the modulus and density, these values are shown in Table 6.3. The densities of the foams are within the range of 28-36 kg/m$^3$. From the literature, the behaviour of polymeric foams within this density range tend to exhibit the following stages under compressive loading: 1) linear elasticity that corresponds to struts bending; 2) non-linear elastic collapse that represents buckling of struts; 3) a plateau region of plastic collapse characterized by plastic hinging of struts; and lastly 4) densification, where a steep increase in stress occurs as the cellular material starts to resemble a solid material. Stages 1-3 can be seen in the sample stress-strain curve for a B130 foam in Figure 6.6. The lower density of the bark foam B130 possibly stems from small amounts of water in the polyol. PEG is a highly hydrophilic polymer; therefore maintaining low moisture content is more difficult than in a polypropylene oxide-based polymer.

Regarding the modulus, in Equations 2.9 and 2.10 the relationships between density and elastic modulus can be seen.[92] The first term ($\rho_s^2$) is based upon the elastic bending of struts. In a closed-cell foam there are additional mechanisms: the second term in Equation 2.10 corresponds to cell membrane stretching, and the last term refers to the contribution from the pressurization of the enclosed gas.[92]. Although the contribution due to gas pressurization is low, the contribution from cell membrane stretching can be significant. It can be estimated that the gas in the cells is at a maximum pressure of 101 kPa, since it foamed at atmospheric pressure but underwent cooling after the reaction. Therefore assuming a pressure of 101 kPa, at a 10% compression, the pressurization of the gas would contribute 10 kPa, or 0.01 MPa, to the value of the modulus. Since the modulus is 2 orders of magnitude larger, we can see that gas pressurization plays a minute role, while the effect of cell face stretching may still have a significant effect. Thus it would be expected that foams with a higher closed-cell content would have a higher elastic modulus. Both control foams had higher values than the bark foams. Since the closed-cell content was much lower in the bark foams (Table 6.3), it corresponds that the modulus values were also lower. Some of the bark samples were non-linear below 5% strain. This could have been due to the uneven distribution of stress, caused by a higher frequency of defects and cell size heterogeneity. Cell heterogeneity would lead to stress concentration at large cells causing their long struts to buckle. The implication of non-linear strains at such low strain is that even low stress levels cause permanent deformation. Therefore it would be expected that their actual compression strength is weaker due to the stress concentration effect and also their response to fatigue would likely be poor.

Stress values at both 10% and 25% strain were used to determine the normalized compression strength of the PUFs. The normalized compression strength is an ideal metric to compare foams since foam strength is proportional to $\rho^2$ as shown in Equations 2.11 and 2.12 for open and closed-cell foams, respectively.[92] Thus, normalizing for density helped to facilitate a better comparison. B90 had the lowest normalized compression strength of all foams, whereas B130 was equivalent to the PEG-G sample. Since compression testing was done in the rise direction, samples that were anisotropic and elongated in the rise direction would buckle more easily. Qualitatively from the optical images in Figure 6.5 it can be observed that PEG-G and PPG-G were more anisotropic than B130, and perhaps this was why B130 performed comparably well, despite having a low value for the closed-cell content and low density. In combination with the swelling, soluble fraction, and glass transition results it would appear that B90 likely had a less cohesive polymer network and poorer morphology compared to B130, and resulted in lower normalized compression strength. It was likely that the higher liquefaction temperature of 130 °C produced larger condensation polymers that created a stable PU network earlier than the many smaller
molecular weight chains produced when liquefied at 90 °C. A more stable network would freeze the morphology and prevent coalescence and Ostwald ripening of cells.

Figure 6.6: A typical stress-strain curve for the bark sample B130, with the 10 % and 25% compression strength strengths indicated as points

Comparisons to the literature can be difficult since researchers use different definitions of compression strength (the value at 10 % will be used hence forth for comparison) and vastly different foam formulations. However, if the isocyanate index and density are similar a comparison may still provide some insight. From Table 6.4 it would appear that despite having liquefied polyols produced from vastly different biomass sources (bamboo[146]/wood[147]/bark) that bark and wood exhibited relatively similar compressive behaviour. Measurements of closed-cell content were not available in the literature, but it was clear from this work that if the amount of closed-cell content were increased it would be an avenue to further enhance the properties of liquefied bark-based PUFs. PUFs produced from blending bark with a polyol resulted in a high normalized strength, primarily due to the very low density foams produced. The low density values reported may be due to rapid catalysis of the polyurethane reaction by using dibutyltin dilaurate as a catalyst. The work done by Hatakayama et al.[148, 149] presents foams with very high compression strengths. Since liquefaction and blending may be used together, this may be an approach to increase the compressive strength, while creating a polyol with even greater biomass content. To summarize, liquefied bark-based polyols have been shown to produce foams with higher normalized compression strength than other liquefied biomass-based polyols and with normalized compression strength within the range of PUFs based upon blends.
### Table 6.3: Comparison of the closed-cell content, density, and mechanical properties of bark-based PUFs to controls

<table>
<thead>
<tr>
<th>foam</th>
<th>closed-cell content (%)</th>
<th>density (kg/m³)</th>
<th>elastic modulus (MPa)</th>
<th>compression strength 10% (kPa)</th>
<th>compression strength 25% (kPa)</th>
<th>normalized strength $\frac{\sigma}{\rho}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPG-G</td>
<td>75.2±0.8</td>
<td>34.9±0.8</td>
<td>3.3±0.1</td>
<td>194±9.3</td>
<td>172±12.1</td>
<td>0.94±0.03</td>
</tr>
<tr>
<td>PEG-G</td>
<td>72.6±2.2</td>
<td>35.5±0.8</td>
<td>3.9±0.7</td>
<td>162±25.2</td>
<td>203±19.1</td>
<td>0.61±0.06</td>
</tr>
<tr>
<td>B90</td>
<td>1.4±1.0</td>
<td>34.6±1.5</td>
<td>1.1±0.1</td>
<td>73±8.5</td>
<td>85±9.4</td>
<td>0.36±0.02</td>
</tr>
<tr>
<td>B130</td>
<td>3.4±1.4</td>
<td>28.8±1.4</td>
<td>1.7±0.1</td>
<td>100±17.5</td>
<td>119±1</td>
<td>0.65±0.07</td>
</tr>
</tbody>
</table>
Table 6.4: A comparison of compression strength data from liquefied biomass-based polyols and from biomass-polyol blends

<table>
<thead>
<tr>
<th>biomass</th>
<th>preparation of polyol</th>
<th>isocyanate index</th>
<th>density (kg/m³)</th>
<th>compression strength (10%) (kPa)</th>
<th>normalized strength $\frac{KPa}{\rho}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>bark[146]</td>
<td>liquefaction</td>
<td>1.1</td>
<td>29-35</td>
<td>73-100</td>
<td>0.65</td>
</tr>
<tr>
<td>bamboo[146]</td>
<td>liquefaction</td>
<td>1</td>
<td>30-35</td>
<td>65</td>
<td>0.23$^d$</td>
</tr>
<tr>
<td>wood[147]</td>
<td>liquefaction</td>
<td>1.2</td>
<td>35-37</td>
<td>70 106$^a$</td>
<td>0.51$^d$</td>
</tr>
<tr>
<td>bark[105]</td>
<td>blend</td>
<td>1</td>
<td>10-20</td>
<td>40</td>
<td>0.87$^d$</td>
</tr>
<tr>
<td>lignin/molasses[148]</td>
<td>blend</td>
<td>1.1</td>
<td>35-70</td>
<td>300-400$^b$</td>
<td>0.99$^d$</td>
</tr>
<tr>
<td>lignin[149]</td>
<td>blend</td>
<td>1.2</td>
<td>60-80</td>
<td>300-400$^c$</td>
<td>0.62$^d$</td>
</tr>
</tbody>
</table>

Variation was from changing the $^a$ liquefaction time; $^b$ lignin-molasses ratio; $^c$ mixing time and only PEG-based data was included
$^d$ Samples with the highest compression strength had their strength values extracted from graphs and then divided by their density
6.3 Conclusions

By systematically comparing bark foams to control foams the effect of the inclusion of liquefied bark bio-polymers could be observed. The liquefied bark compounds exert their influence through their hydroxyl type and hydroxyl value depending on the liquefaction temperature. This can vary the foaming kinetics due to differences in heat evolved from different alcohols and also difference in their abundance. Analysis using dynamic mechanical analysis (DMA) showed glass transition temperatures were within a comparable temperature range of 145-160 °C. The bark foams exhibited less intense tan δ peaks, which implied the presence of high functionality compounds that enabled elastic behaviour, but restricted viscous flow. The presence of liquefied bark compounds was found to cause a high amount of open-cell content. This is of importance since the modulus of both bark foams were lower than the controls and closed-cell content has a role in the elastic behaviour due to membrane stretching and gas pressurization. This may have been due to the presence of low molecular weight compounds with low functionality, and resulted in unstable membranes that ruptured. This may be remedied by removing these low functionality / degradation products or alternatively by optimization of the formulation and amount/type of surfactant used. The soluble fraction of the bark foams was also higher than the controls and confirmed the presence of low functionality, low molecular weight compounds. Furthermore, bark foams have a less well defined morphology compared to the controls that indicated the bark polymers could have lower surface tension resulting in unstable cell growth and expansion, or took longer to form a stable polymer network. These results show that in most aspects the presence of bark does not negatively impact the properties, but does exert an influence on cell morphology and open-cell content.

By comparing the two bark foams, B90 and B130, to each other the effect of liquefaction temperature on foam properties could be observed. The bark foam B130 that was produced from the polyol produced at a higher liquefaction temperature demonstrated a higher elastic modulus and higher compression strength, while at a lower foam density. The greater fraction of high molecular weight compounds, with likely greater functionality, was presumably the reason. In contrast, the P90 polyol used to produce the B90 foam had a large amount of small molecular weight compounds that proved to be deleterious to foam properties. This research showed that liquefaction of bark can produce foams with similar characteristics to a control sample, has identified areas for formulation optimization, and has shown that liquefaction temperature is a key determinant of foam characteristics.
Chapter 7

The alkoxylation of bark and bark extractives

The following work has been adapted from the journal of Industrial Crops & Products:


7.1 Introduction

Liquefaction at high temperature has been common practice to achieve a high conversion yield. It has been shown in the literature that liquefaction at 150 °C was used to produce flexible PUFs,[54, 60] and liquefaction under harsher conditions of above 200 °C was also performed.[61] However, at high temperatures extensive degradation can occur, especially to sugars.[64] In the work presented above, liquefaction was done at milder temperatures, and the polyols produced foams with compression strength comparable to control foams. But, the presence of low molecular weight compounds may have negatively affected both the closed-cell content and network formation.[118] Therefore, even mild liquefaction still resulted in a large amount of low molecular weight compounds, possibly with low functionality, which negatively affected foam properties.

Due to the aforementioned limitations of liquefaction, an alternative approach is to utilize alkoxylation to modify bark directly. Alkoxylation, or more specifically oxypropylation, is to chain extend molecules with hydroxyl functionality through a base-catalyzed anionic ring-opening polymerization of propylene oxide (PO) to form polypropylene glycol (PPG) polyols. This is an appealing process since it can be done under mild alkaline conditions that will result in less degradation of sugars compared to the strongly acidic and oxidizing conditions experienced during liquefaction;[64] the high pressure and temperature produce high yields;[69] and most importantly, the alkoxylation of sugar, glycerol, and short glycols is already a common practice in industry to produce polyols.[84] The reported procedures for alkoxylation are quite varied, such as room temperature reactions in solvent,[78] pressure controlled reactions through gradual addition of PO monomer into the reactor, [71] and higher pressure/ higher exothermic reaction conditions that utilized PO as a solvent. Alkoxylation has already been performed on a variety of biomass
resources such as chitin/chitosan,[74] cork,[70] date seeds,[73] lignin,[75, 77, 144] inulin,[150] starch,[71] sugar beet,[72], tannin[151, 78] and terpenes.[152] Although lignin and tannins are both components in bark, bark has a wide variety of other extractive compounds and therefore its alkoxylation behaviour could vary significantly from what has been reported previously by the literature. Furthermore, the previous work done on tannins was performed at room temperature,[78] as opposed to 180 °C in this work. The work done by Arbenz et al. contrasted the oxybutylation behaviour of different tannins and showed that a 100 % bio-based polyol could be synthesized by using biosourced butylene oxide, instead of propylene oxide.[151]

Despite the high temperature and pressure of alkoxylation it can still be difficult to achieve penetration through the cell walls of the bark. One solution could be to treat bark with alkaline solution to cleave the lignin matrix and thereby improve accessibility and reduce molecular weight. Alkaline treatments have been shown to solubilize phenolic compounds, swell the biopolymer matrix, and reduce crystallinity.[30] These extracts have been studied previously when preparing bark-based resins for adhesives.[153, 31, 154]

This study will focus on the oxypropylation behaviour of bark and an alkaline extract of bark, and then characterize the bark-based polyols to evaluate key parameters for their use in PUFs. The specific goals of this research are twofold. Firstly, alkaline extracts of bark will be compared to untreated bark and a control based upon their oxypropylation behaviour and polyol properties. Since the oxypropylation of bark has not been reported previously, nor of the alkaline extract of bark, this work will provide insight into how bark compares to other biomass feedstocks. Secondly, key polyol characteristics, such as the hydroxyl value, hydroxyl type, viscosity, and molecular weight will be characterized. Often in the literature, research has focused more upon foam properties, without thorough characterization of the polyol. In this work phosphorus NMR was used to determine the type of alcohols present which affects the reaction rate with isocyanate. The polymer structure was probed through gel-permeation chromatography, viscometry, and thermo-gravimetric analysis. Finally, proton and carbon NMR were used to examine the presence of polymerization side-products and composition. This kind of characterization is essential in order to assess the potential of bark-based polyols for producing rigid foam products.

### 7.2 Results and Discussion

**Characterization of Bark and Alkaline Extracts of Bark**

*Pinus contorta* bark has a high concentration of extractive-type compounds that are accessible and can be oxypropylated. Based on oven dry bark, successive solvent extractions resulted in a total extractives content of 75 %. Benzene extractives accounted for 28.7 % (terpenes, fats, waxes, sterols, resins), alcohol for 10.9 % (polyphenols, tannins, mono and di-saccharides), hot water for 5.6 % (starch, pectins, mucilages), and lastly 1 % NaOH for 29.8 % (phlobaphenes, phenolic acids, lignin, hemicelluloses, and suberin). The non-extractives consisted of roughly 19 % polysaccharides and 5 % lignin.[2] Alkaline extracts of *pinus contorta* bark were previously characterized by our group using C-NMR and shown to be composed of tannin, fragmented lignin, and degraded hemi-cellulose.[155, 154] It can be seen from the thermo-gravimetric analysis of bark in Figure 7.1 that the low-temperature stability of the extractives and polysaccharides results in degradation at approximately 240 °C. Since the alkaline extract of bark has a high concentration of extractives the degradation behaviour was more pronounced earlier. However, the alkaline extracts of bark also contain a high concentration of lignin fragments and phenolic extractives,
resulting in a 48 % residue at 700 °C, while the regular bark has only 18 %. In combination with the previous NMR results, this conclusively showed that alkaline extractives contained many temperature stable aromatic structures that would be beneficial to incorporate into a polyol.

Figure 7.1: The mass loss due to heating of the initial bark and the alkaline extract of bark

Bark oxypropylation

Biomass Conversion Yield:

Oxypropylation would be expected to begin with the most easily accessible components, the extractives. This explains why a high yield of 79 % was attained after only two hours for bark. To gain access to the reducing sugars (crystalline cellulose) and lignin, harsher oxypropylation conditions or a longer reaction time may be needed. In addition, alkaline extracts of bark of other relevant species have been studied previously in the literature and have been shown to improve accessibility and increase the concentration of phenolic compounds. Alkaline treatment of *pinus oocarpa* greatly reduced the molecular weight to less than 10,000 Da.[26] Work done on alkaline extracts of *pinus pinaster* bark showed that the treatment concentrated the amount of klason lignin from 30 % in the pristine bark to 44 % in the extract. [156] In addition to lignin, alkaline extracts of *pinus pinaster* bark were shown to be composed of gallic acid and catechin equivalent phenolic structures.[157] From these previous results and our previous work [155, 154], it was expected that the alkaline extracts of (*pinus contorta*) would be more accessible than the pristine bark and that the polyols would have a high concentration of phenolic compounds.

The oxypropylation results in Table 7.1 showed that the alkaline extracts of bark had a lower conversion yield (32 %) and reduced consumption of PO (66 %) compared to the regular bark (79 % and 75 %, respectively). This indicated a less conducive material for the oxypropylation reaction. The alkaline treatment to produce the extract can degrade glucose into various acids like saccharinic acid, lactic acid, or formic acid.[158] Furthermore, C-NMR and FTIR analysis revealed that alkaline extractions on lignin yield aliphatic carboxyls.[35] Glasser et al. have shown in previous work that the reaction is retarded by the acidity of a hydroxyl group according to the following trend: aliphatic OH < phenolic OH < COOH.[76] Therefore, these acidic groups may have retarded the reaction rate[68], as a result the oxypropylation and monomer conversion is lower, despite the extract being more accessible.

Characteristics of the Oxypropylation Reaction  Bark and alkaline extracts of bark were
Table 7.1: Reaction and polyol characteristics

<table>
<thead>
<tr>
<th></th>
<th>control</th>
<th>bark</th>
<th>alkaline bark extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>biomass conversion yield (wt.%)</td>
<td>-</td>
<td>79</td>
<td>32</td>
</tr>
<tr>
<td>PO conversion (%)</td>
<td>92</td>
<td>75</td>
<td>66</td>
</tr>
<tr>
<td>maximum temperature (°C)</td>
<td>240</td>
<td>222</td>
<td>204</td>
</tr>
<tr>
<td>$T_{Max}/\Delta t$ (°C/min)</td>
<td>21.8</td>
<td>13.1</td>
<td>13.6</td>
</tr>
<tr>
<td>homopolymer content (wt.%)</td>
<td>-</td>
<td>51</td>
<td>63</td>
</tr>
<tr>
<td>hydroxyl value (mgKOH/g)</td>
<td>-</td>
<td>444±7</td>
<td>408±4</td>
</tr>
<tr>
<td>polyol bark fraction (wt.%)</td>
<td>-</td>
<td>38</td>
<td>18</td>
</tr>
</tbody>
</table>

*a* This value is based upon the residual pressure after two hours; it is assumed that PO is the sole contributor to the pressure, although water may be present.

*b* The pressure values reported included the 50 psi contribution from $N_2$ that was used to fill the vessel.

*c* Based upon the biomass conversion yield and the PO conversion.

Oxypropylated and their temperature and pressure profiles can be seen in Figure 7.2a and b, along with a summary of the reaction and polyol characteristics in Table 7.4. In order to contrast the reactivity of bark and the alkaline extracts of bark, polyethylene glycol 400 was oxypropylated under identical reaction conditions. Two key observations regarding the pressure and temperature during the reaction are quite informative and showcase the behaviour of bark oxypropylation. Firstly, in Figure 7.2a, throughout the entire reaction the control sample maintained a lower maximum pressure (340 PSI) than the two bark samples (470, 450 PSI). This is reflected by the fact that the control sample had a greater conversion of the monomer (92 %) than the bark samples (75 %, 66 %). This indicated that the PO was consumed quicker in the control reaction and therefore the PO partial pressure was less. Secondly, from Figure 7.2b, the control sample reached a higher maximum temperature of 240 °C while the bark samples only reached 222 and 204 °C. Also, the exothermic rate of heating was higher in the control sample (21.8 °C/min) than the bark samples (13.1, 13.6 °C/min). These observations corroborated with the previous finding that the PO was consumed quicker in the control sample. This occurred to such an extent that the exothermic heat generated a significantly higher reaction temperature than the bark samples. These observations show that bark is less reactive than the control. The control is a liquid and bark is a powder, therefore the lower reactivity of bark compared to PEG could be due to the lower accessibility of the bark (especially since bark contains recalcitrant crystalline cellulose within a lignin matrix). Another contributing factor could be the retardation of the reaction caused by acidic groups.[76] The presence of fatty acids is unlikely since they have been removed through the hexane extractions during the preparation of the bark powder; however higher molecular weight acidic terpenoids could be present.

**Comparison to other types of Oxypropylated Biomass:** Since a variety of biomass have been oxypropylated previously a comparison may provide some insight into the relative effectiveness, despite the diversity of reaction conditions used, such as the biomass/PO ratio, reaction time, catalyst
concentration, and set-temperature. In a review paper it was shown that rapeseed cake achieves complete conversion, with no residues, at a lower temperature and shorter duration. Using a higher temperature of 200 °C, olive stones were able to be completely liquefied with no residues. Finally, certain types of lignin like soda or organosolv could be completely liquefied, whereas kraft lignin was more resistant. This shows that the bark in this work is more difficult to liquefy than certain types of biomass, but compared to some types of lignin it showed comparable yields. It is possible that using higher temperature, longer time, and a lower bark/PO ratio may achieve complete conversion of the bark. However, other aspects like the polyols viscosity and hydroxyl values must also be considered. Polyols for rigid foam formulations generally have an hydroxyl value (OHV) from 300 - 600 mgKOH/g and a viscosity from 2000 - 50000 cP, both of which are amply satisfied by the bark-based polyols produced in this work.

Thermo-gravimetric analysis (TGA) of the Polyol Components

The derivatives of TGA graphs can be insightful for probing the components of a polyol. The process of oxypropylation produces two components as shown in Figure 7.3. Initially, KOH reacts with bark to produce an alcololate and releases water, as shown in reaction 1. The alcololate reacts with PO to produce the copolymer phase (bark compounds with grafted polypropylene glycol chains) as shown in reaction 2a and 3. Water released from the reaction with KOH and bound water present in the bark react with PO to produce the homopolymer phase (polypropylene glycol diols) as shown in reaction 4.

From Figure 7.4a it can be seen that both polyols have two degradation maxima; one at a high temperature of 380 °C and another below 300 °C. These two regions can be attributed to the two components in the polyol, the copolymer phase and the homopolymer phase. It was shown by Pavier et al. that refluxing the polyol in hexane was an effective method for separation of the two phases. The copolymer was insoluble, while the homopolymer was extracted by the hexane. The graphs of the copolymer fraction in Figure 7.4b show that the bark components have a broad degradation peak at 380 °C. This is consistent with researchers who have shown that larger bio-polymers like hemi-cellulose, cellulose, and lignins start to breakdown at 280-330 °C, 350 °C, and 450 °C, respectively.
Figure 7.3: Various hydroxyl containing compounds (R= sugars, tannins, terpenoids, and lignins) found in bark that 1) react with KOH to form an alcoholate and water. 2a and 4) PO reacts with the alcoholate to form polypropylene glycol chains grafted onto the bark compounds and 3) PO reacts with water to form polypropylene glycol diols. 2b) A chain transfer side-reaction can occur where the growing chain is terminated through abstraction of a proton from the monomer. The monomer then rearranges and has an unsaturated end-group. This reaction can be minimized through the use of ligands (L).
minute peak at 150 °C present in the copolymer would seem to indicate that the bark components have some degree of polypropylene oxide grafting. This result provided evidence of grafting through propoxylation since a hexane extraction could not separate the highly soluble glycol chains from the bark biopolymers.

Regarding the homopolymer fraction in Figure 7.4c, a difference can be observed between the oxypropylated bark (OP-B) and the oxypropylated alkaline extracts of bark (OP-AB). OP-B exhibited one peak (180 °C), while OP-AB has two peaks (150 °C and 250 °C). The presence of two peaks in the homopolymer fraction of OP-AB suggests that homopolymers of PPG and PPG grafted onto low-molecular weight bark compounds are present. The alkaline extracts of bark likely had many simple phenolics and sugars with PPG chains that make it highly soluble in hexane. H-NMR was done on the homopolymer and from Figure 7.5 some aromatic protons could be observed, especially in the homopolymer from the alkaline extract.

![Graphs](image)

**Figure 7.4**: The differential thermo-gravimetric curves of both oxypropylated bark (OP-B) and oxypropylated alkaline extracts of bark (OP-AB) a) polyols, and separated into the b) copolymer and c) homopolymer fractions

To summarize, alkaline extraction may have produced some lignin fragments that were then oxypropylated with PPG chains that made them highly soluble. Even the breadth of the OP-AB polyol peak
Figure 7.5: The aromatic proton region of the H-NMR spectra of OP-B and OP-AB homopolymer fractions. The large amount of peaks indicates that small aromatic compounds were propoxylated to make them soluble in hexane.

would seem to imply that the homopolymer fraction is not simply PPG chains, but PPG grafted onto a variety of lower molecular weight substrates. Many papers have used solvent-extraction as a way to assess the homopolymer and copolymer fractions, but this work showed that the differentiation between the two was not as evident as it may have seemed. This work showed that three fractions were found in the polyols: homopolymers of PPG soluble in hexane, small molecular weight bark compounds with PPG grafts that are soluble in hexane, and high molecular weight bark compounds with PPG grafts insoluble in hexane.

**NMR Analysis**

Although H-NMR can be difficult to interpret due to the confluence of peaks within a narrow ppm range, it can be seen from the spectra in Figure 7.6a and b that the bark polyols differ considerably from a polypropylene glycol polymer (PPG-425). This is most evident in the regions related to carbons bonded to oxygen and unsaturated carbons.

When looking at the region known for hydroxyl groups in Figure 7.6a it can be seen that the PPG sample has a strong peak at around 4.4 ppm, while the two bark samples show a greater diversity of hydroxyl groups from 4.3-4.6 ppm. This implied that although some of the hydroxyl functionality is from the end-groups of the polypropylene chains, there were also hydroxyl groups present from bark components that could be primary and secondary alcohols, and confirmed by the P-NMR results in this work.

More interesting were the protons from unsaturated carbons occurring in three regions: linear alkenes from 4.8-5.3 ppm, cyclic alkenes from 5.8-5.9 ppm, and aromatics from 6-8 ppm. The linear alkenes (lower ppm peaks) could have a variety of origins. 1) They could be due to fatty acids from the bark that were not leached during the hexane extraction during the preparation of the ground bark powder; 2) from double bonds present in terpenoids like epimannol found in *Pinus contorta* bark;[2] or 3) from side-reactions of PO that form allyl or propenyl moieties. The formation of allyl or propenyl groups is supported by the fact that peaks labelled in Figure 7.6a are consistent with protons in the methyl group (1) of the propenyl moiety near 2 ppm. As well, terminal protons of the propenyl (2) and allyl group (3). These allyl and propenyl groups can be formed during oxypropylation. The alcoholate primarily
reacts with PO to form a growing polymer chain, but under certain conditions PO acts as a ligand for the alcoholate and abstracts a proton from the methyl of PO. A chain transfer reaction to the monomer occurs, resulting in a rearrangement that yields an allyl alcohol, or a further rearrangement to produce propenyl alcohol as shown in reaction 2b of Figure 7.3. This unwanted side reaction reduces polyol functionality since an unsaturated end-group is formed instead of a hydroxyl end-group. As shown in reaction 2a, this rarely happens in polymerizations where a low amount of PO is used relative to the seed compound. This is because hydroxyl groups act as a better ligand than PO for the alcoholate.[68] Therefore, the high concentration of hydroxyls in bark and their lone pairs complexing with potassium reduced the prevalence of the chain transfer reaction.

The typical method to determine unsaturation based on titration with mercuric acetate would not be suitable since many natural bark compounds like terpenoids and fatty acids also contain alkenes. Therefore, it is likely that some end-groups have unsaturated ends, but it did not occur to large extent since the intensity of the peaks were low. Furthermore, the literature has shown that polyols that have a high OHV ranging from 300-800 mgKOH/g possessed a low amount of unsaturated groups ranging from 0.005-0.01 meq/g.[68] The hydroxyl value for AB was 444 and for AAB was 408 mgKOH/g, and therefore the amount of unsaturation was likely low due to the ligand effect of hydroxyls during the polymerization. On the contrary, long chain glycols like PPG-2000 can have up to 4-20 olefinic terminal end-groups per 100 molecules.[79] This should serve as a precaution for future work. If the reaction temperature were increased to achieve a higher conversion or if a higher PO to biomass ratio were employed these changes could promote the formation of olefinic end-groups.[79] This is an aspect not often discussed in the alkoxylation of biomass, yet is important because non-reactive end groups can be detrimental to the network-forming potential of a polyol.

Aside from the linear alkenes, protons at higher ppm shifts from 5.8-5.9 ppm were also observed in the magnified spectra of Figure 7.6b and are consistent with the double bonds found in non-aromatic cyclic structures. These are expected due to the high concentration of higher terpenoids like sesquiterpenes in bark.[160] Finally, it can be seen from the magnified image in Figure 7.6b that a variety of aromatic protons exist in the two bark-based polyols. Due to inherent differences in signal intensity between C-NMR and H-NMR, this shows that a great variety of aromatic rings are present, even though the C-NMR in the following section showed only a few aromatic carbons.

C-NMR was performed on the polyols and the spectra can be seen in Figure 7.7. It is evident that both polyols OP-AB and OP-B were very similar to a PPG-425 sample. The carbons in the main chain of a polypropylene glycol were consistent with the following observed peaks: CH$_3$: 17.1 - 17.3 ppm; CH$_2$: 72.1 - 72.4 ppm; CH: 74.2 - 74.6 ppm.[161] Due to the presence of a hydroxyl group on the terminal units, carbons on an end group have peaks observed at CH$_3$: 20.3 ppm; CH$_2$: 76.7 ppm; CH: 65.2 - 65.4 ppm. Although not quantitative, it can be seen from the relative peak intensity of a methylene carbon to a methylene end-group or methine carbon to a methine end-group, that the oxypropylated bark polyols have a greater fraction of carbons on the end-groups compared to the PPG-425 sample. This implied a considerable amount of end-groups were present in the oxypropylated polyols, implying shorter chain lengths than PPG-425. The diol PPG-425 had a degree of polymerization of approximately seven, which meant that the bark compounds likely have shorter oligomeric PPG-chains grafted onto them.

Performing P-NMR on phosphitylated polyols has proven to be a facile method to determine the type and quantity of hydroxyl groups present. Bio-based polyols are rarely characterized in this manner; however the type of hydroxyl groups present in the polyols has a large impact on the polyurethane
Figure 7.6: The magnified H-NMR spectra of PPG, OP-AB, and OP-B polyols that showed a) hydroxyl groups and linear alkenes; and b) the presence of aromatic and cyclic alkenes in the bark polyols.

Figure 7.7: C-NMR spectra of PPG-425, oxypropylated alkaline extracts of bark (OP-AB) and alkoxylated bark (OP-B) polyols, peaks with an asterisk represent carbons on the hydroxyl end unit.
reaction and temperature stability of the PUF. The ppm shifts of different alcohols when phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane are roughly as follows: phenolics: 143 − 137 ppm; aliphatic: 148 − 145 ppm. Firstly, it can be observed that only aliphatic alcohols were present since no peaks were observed within the range of 143 − 137 ppm. Phenolic groups form thermally labile urethane linkages. Therefore, it was ideal that oxypropylation is able to convert these through chain extension into aliphatic hydroxyl groups.

Regarding aliphatic alcohols, secondary alcohols will tend to be at lower ppm shifts than primary alcohols. From Table 7.2 it can be seen that the polymerization of PO onto bark compounds has produced a polyol with roughly four times more secondary hydroxyls than primary hydroxyls. The polymerization of PO under basic conditions will produce a variety of isomers adorned with typically 94 - 96 % secondary hydroxyls, and 4 - 6 % primary hydroxyls.[68] Since the type of hydroxyl group can impact the reaction kinetics of a polyol with isocyanate this is an important aspect to characterize when utilizing biomass to make a polyol. Compounds like polyethylene glycol (PEG-400), polypropylene glycol (PPG-425), and dipropylene glycol (DPG) were phosphitylated to facilitate assignments. It can be observed from Figure 7.8 that both oxypropylated polyols have secondary hydroxyls in between 145.5 - 145.8 ppm and very minute primary hydroxyls peaks from 147.6 - 147.8 ppm. These were consistent with the DPG and PPG-425 samples studied. The two distinct peaks found only in the bark polyols were the primary hydroxyl at 147.35 ppm and the secondary hydroxyl at 145.7 ppm. These peaks may be attributed to bark compounds with sterically hindered hydroxyls that could not undergo oxypropylation.

In summary, the bio-polyols have a hydroxyl value in the 400 mgKOH/g range and consist of roughly 80 % secondary alcohols, 20 % primary alcohols, and no phenolic alcohols. In contrast, polyols produced through liquefaction using acid-catalyzed glycolysis typically have a high concentration of primary alcohols since glycerol and polyethylene glycol are used as the solvent.[118] Primary alcohols react very rapidly with isocyanate[22, 23] and phenolic alcohols produce temperature unstable urethane linkages.[24] For these reasons it can be seen that the oxypropylation of bark produced hydroxyl groups that are preferred in polyols for rigid foam formulations.

Figure 7.8: The P-NMR spectra of oxypropylated alkaline extracts of bark (OP-AB) and oxypropylated bark (OP-B) compared to dipropylene glycol
Table 7.2: Hydroxyl type and quantity from the P-NMR phosphitylation method

<table>
<thead>
<tr>
<th>Type</th>
<th>OP-B</th>
<th>OP-AB</th>
</tr>
</thead>
<tbody>
<tr>
<td>aliphatic primary</td>
<td>84</td>
<td>76</td>
</tr>
<tr>
<td>aliphatic secondary</td>
<td>328</td>
<td>383</td>
</tr>
<tr>
<td>hydroxyl value (mgKOH/g)</td>
<td>412</td>
<td>459</td>
</tr>
</tbody>
</table>

Viscosity and gel permeation chromatography (GPC) analysis

Viscosity and molecular weight are key characteristics of a polyol. Although both are intrinsically linked, viscosity has an indirect effect by determining both how well a polyol mixes with an isocyanate and bubble growth kinetics. Molecular weight will determine the distance between cross-links within a thermoset. The viscosity of the two polyols and their molecular weight characteristics are detailed in Table 7.3. It is evident that there is a large difference in the viscosity of the two polyols, with the OP-B polyol being substantially higher; despite the two polyols having comparable values for their weight average molecular weight (M<sub>w</sub>) and number average molecular weight (M<sub>n</sub>). This may be explained by the low concentration of bark in the OP-AB sample (due to a low biomass conversion yield) and therefore it consisted of more linear chains. While the OP-B polyol had a higher biomass conversion yield and will have had a higher functionality, and therefore a higher viscosity. Compared to the viscosity of other oxypropylated biomass, oxypropylated bark was within the lower range of the viscosity values. For example the work done on chitosan exhibited an extremely high viscosity of 50,000,000 cP,[74] cork: 3000 - 13000 cP,[162], lignin: 2300 - 2,800,000 cP,[77], and tannin: 1000 - 250,000 cP.[151] This range in values is likely impacted by the type of biomass, but also a very strong dependence on the reaction conditions. Low viscosity values indicate that a high amount of homopolymer existed since they can act as plasticizers. This was beneficial since high viscosity polyols can be troublesome to utilize solely and require blending with a lower viscosity polyol.

Table 7.3: GPC and viscosity data of the oxypropylated bark polyols OP-B and OP-AB

<table>
<thead>
<tr>
<th></th>
<th>OP-B</th>
<th>OP-AB</th>
</tr>
</thead>
<tbody>
<tr>
<td>M&lt;sub&gt;n&lt;/sub&gt; (Da)</td>
<td>475</td>
<td>855</td>
</tr>
<tr>
<td>M&lt;sub&gt;w&lt;/sub&gt; (Da)</td>
<td>6821</td>
<td>7110</td>
</tr>
<tr>
<td>PDI</td>
<td>14.36</td>
<td>8.32</td>
</tr>
<tr>
<td>viscosity (cP)</td>
<td>6000</td>
<td>980</td>
</tr>
</tbody>
</table>

The GPC data in Figure 7.9 showed that a broad plateau of molecular weights existed from about 1000 - 5000 Da. Below this was a tail of compounds of less than 1000 Da that produced a low value of M<sub>n</sub>. However, the very large molecular weight tail of the polyols likely biased the value of M<sub>w</sub>, and resulted in an average of approximately 7000. The oxypropylated bark appeared to have slightly higher values for the number and weight average molecular weight. This disparity between the M<sub>w</sub> and M<sub>n</sub> was further exemplified by the extremely large values of the polydispersity index (PDI).

Typically PDI indicates how controlled the polymerization kinetics are with highly controlled polymerization having PDI values of <1.1. Since the seed compounds (bark/alkaline extracts of bark) were very diverse in molecular weight, it was expected that the oxypropylated polyols would also have produced a large PDI. One advantage of using an alkaline extract of bark was that since it underwent alkaline hydrolysis, that process homogenized (relative to bark) the molecular weight profile, and produced a
Chapter 7. The alkoxylation of bark and bark extractives

substantially lower PDI.

Another observation was related to the solubility of the polyols observed when GPC samples were prepared. Compared to liquefied bark, oxypropylated bark had far greater solubility in organic solvents like THF. This enabled facile characterization; unlike the acid-catalyzed liquefied bark polyols that required a benzoylation reaction to improve solubility.[117] Liquefied bark-based polyols also tended to sediment over time; however this was not the case with oxypropylated bark-based polyols. Therefore, chain extension with PO was highly effective, since high molecular weight compounds were made more soluble.

The $M_n$ values were within a suitable range for a rigid polyol although it is clear that the $M_w$ values are skewed due to the significant portion of the polol being within the high molecular weight tail of the distribution. These larger polymers may be due to the presence of either long polypropylene glycol chains or large molecular weight bark molecules with high solubility. The first case was unlikely since the ratio of PO to bark was quite low and the C-NMR data showed qualitatively that the signal intensity for carbons on the end-group was comparable to the intensity of carbons on the main chain. This would only be the case if the grafted PPG-chains were oligomeric in nature. By grafting large molecular weight bark molecules with PPG chains the solubility was greatly increased.

Finally, few papers have performed GPC analysis on their polyols for comparison; however a study done on oxypropylated lignin shows $M_w$ and $M_n$ values are within a similar range, and that by changing the biomass/PO ratio and catalyst amount these values can be tuned.[75] This is supported by the GPC analysis of oxybutylated gambier tannins where the tannin/butylene oxide ratio varied the molecular weight from 3000-7000 Da and the homopolymer from 200-900 Da.[151] These literature results stress the fact that reaction conditions can be varied to tailor-make polyols and provide an opportunity for future optimization and customization.

Figure 7.9: GPC profiles of oxypropylated bark (OP-B) and oxypropylated alkaline extracts of bark (OP-AB) polyols.

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Foaming and Compression Testing

To demonstrate the potential of oxypropylated bark-based polyols for making a rigid PUF, a preliminary investigation into their foaming behaviour was done. The mechanical properties of the OP-B polyol were
contrasted to previous results of a control foam and foam made from liquefied bark.[118] The control foam is a 9:1 blend of PPG-425 with glycerol. It can be seen from Table 7.4 that the oxypropylated foam exceeded both samples in elastic modulus and compression strength, and that even when normalized for density the oxypropylated bark-based foam was superior. The normalized compression strength was based on equation in Ashby et al. that makes compression strength proportional to density\(^{1.5}\) for a closed-cell foam.[92] Oxypropylation was a grafting/polymerization reaction, whereas liquefaction was an inherently degradative process. The combination of a higher molecular weight, less degradation, and a higher bark fraction due to a higher biomass conversion yield, have all led to a polyurethane network that was superior to that made from a liquefied bark-based polyol. Furthermore, the oxypropylated bark showed improved mechanical properties over oxypropylated lignin PUFs with an elastic modulus of 3.41 MPa;[75] oxypropylated kraft lignin PUFs with a strength value of 140 kPa and modulus of 3.41 MPa;[163] and a lower modulus, but comparable strength to PUFs made from oxypropylated organo-solv lignin.[164] The oxypropylated bark PUF however had a lower elastic modulus and strength than foams made from liquefied starch that was then oxypropylated.[71] These comparisons show that oxypropylated bark was quite promising and with future work the mechanical performance and other key properties can be studied in greater detail and improved.

Table 7.4: The mechanical properties of a control foam contrasted to the alkoxylated bark-based foam

<table>
<thead>
<tr>
<th>foam</th>
<th>density (kg/m(^3))</th>
<th>elastic modulus (MPa)</th>
<th>compression strength 10% (kPa)</th>
<th>normalized strength (\frac{\sigma}{\rho}^{0.5})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPG-G(^a)</td>
<td>34.9±0.8</td>
<td>3.3±0.1</td>
<td>194±9.3</td>
<td>0.94±0.03</td>
</tr>
<tr>
<td>B130(^b)</td>
<td>28.8±1.4</td>
<td>1.7±0.1</td>
<td>100±17.5</td>
<td>0.65±0.07</td>
</tr>
<tr>
<td>OP-B</td>
<td>23±4</td>
<td>5.5±0.8</td>
<td>267±4</td>
<td>1.3±0.3</td>
</tr>
</tbody>
</table>

\(^{a}\) The PPG-G polyol consisted of a 9:1 by weight blend of PPG-425 and glycerol
\(^{b}\) B130 is a bark-based foam made from the liquefaction of bark at 130 °C as reported in previous work.[118]

### 7.3 Conclusions

The oxypropylation of bark and an alkaline extract of bark have produced some interesting differences in oxypropylation behaviour and polyol structure. Bark was oxypropylated far easier than the alkaline extract of bark, with 79 % being converted versus the extract that had a yield of 32 %. The higher concentration of phenolics and acids in the alkaline extract retarded the reaction rate. Complete conversion may be possible with longer reaction times and a lower bark/PO ratio. The alkaline extract of bark had a greater diversity of hexane soluble compounds found in the homopolymer compared to the pristine bark. This could be due to the presence of cleaved biopolymers like lignin fragments produced by the alkaline treatment and then grafted with PPG chains.

The characterization of the bark-based polyols provided some key insights into the polyols structure. Firstly, it was shown through H-NMR that protons consistent with propenyl and allyl groups were present. This was an important aspect since the high temperature needed to overcome the glass transition temperature of lignin and using KOH as a catalyst could have promoted the formation of terminal unsaturation, and thereby lowered the overall functionality of the polyol. However, their small peak
intensity indicated that terminal unsaturation did not occur to a large extent. The low ratio of PO to seed compounds would have also resulted in unfavourable reaction conditions for the unsaturation to be significant due to the ligand protection effect of hydroxyl groups. Secondly, through solvent extraction it was found that the homopolymer acted as a plasticizer for the copolymer. As a result, the bark polyols have a very low viscosity, especially compared to work done on other types of biomass that produced prohibitively highly viscous liquids. Thirdly, GPC analysis showed that the polyol was highly polydisperse and contained very high molecular weight molecules. This indicated that typically insoluble bark compounds were made soluble through the grafting of PPG chains. Lastly, the $M_n$ values, the hydroxyl value, and high concentration of secondary alcohols were in line with those of typical commercial polyols used for rigid foam formulations. When used to make a polyurethane foam, the oxypropylated bark-based foam showed superior mechanical properties to previous work done on liquefied bark and a polypropylene glycol control foam. These results helped to elucidate some of the complex changes made to bark biopolymers during an oxypropylation reaction.
Chapter 8

Conclusions

To focus the many ideas and results discussed in the above chapters into a more concise concluding message the work has been summarized, the main contributions of this work have been detailed, and lastly some broader concluding statements are made about the implications of this work.

Summary

This study on the conversion and characterization of bark-derived polyols has provided many insights, has opened new avenues of investigation, and has provided a framework for future investigations into the utilization of bark. In chapter 4 and chapter 5 a systematic analysis and detailed characterization showed how polyol structure changes through altering liquefaction temperature and solvent. It was shown in chapter 6 that if network formation and closed-cell content were increased that the liquefied bark based foams would exhibit improved compressive behaviour. Finally, in chapter 7 it was shown that alkoxylation could be used to achieve a high conversion yield, produce a high molecular weight polyol with minimal degradation, and a foam with high compression strength.

In chapter 4 it was shown that liquefaction temperature had a significant effect on polyol characteristics. Previous work in the literature had simply shown increasing liquefaction temperature as a means to increase conversion yield, without evaluating its influence on the polyol properties. Above 90 °C sugars were found to degrade into levulinate and formic esters; compounds with low functionality and low molecular weight. Furthermore, $^{31}$P-NMR revealed that liquefaction at 90 °C preserved the secondary alcohols of sugars, while at higher liquefaction temperature the polyols mostly consisted of primary alcohols. Characterization of the molecular weight profiles of the polyols produced at three liquefaction temperatures (90, 130, 160 °C) revealed a highly poly disperse material owing to the decrease in molecular weight due to chain cleavage from glycolysis/hydrolysis reactions and the increase in molecular weight due to condensation reactions between biopolymers. Low molecular weight compounds tend to have low functionality. At 90 °C there are many small compounds produced via scission of biopolymers and at 160 °C many small compounds were produced due to degradation. High molecular weight compounds tend to have low solubility and precipitate. At 160 °C many of these were found due to the high temperature promoting condensation reactions that rapidly increased molecular weight. These results provided the foundation for understanding the foam properties evaluated in chapter 6 and was the rationale for the following work only conducting liquefactions at 130 °C. Finally, it was also found that phenolic structures from the extractive compounds were grafted with the glycols in solution.
to form aromatic structures with aliphatic alcohols, a beneficial feature for making stable polyurethane linkages.

In chapter 5 it was shown that the liquefaction could be kept at a moderate temperature of 130 °C and that through solvent selection the yield and the extent of degradation could be altered. This was done through a comprehensive study using composition and elemental analysis of residues and H-NMR of polyols by utilizing a variety of polyhydric alcohols and organic solvents. Polyhydric alcohols with low equivalent weight and primary alcohols produced a highly polar solvent environment that improved conversion and also reduced the formation of acid-insoluble lignin (AISL) products. This was likely due to the formation of a protective solvation shell. Secondary alcohols were also shown to decrease the hydroxyl value of the polyol, which lent support to the theory that primary alcohols had a role to play in preventing condensation reactions. By varying the organic solvent it was found that ketones with highly charge separated structures like acetyl acetone and cyclohexanone were able to improve conversion and reduce AISL formation. This was ascribed to the ability of these solvents to act as proton acceptors and engage in hydrogen bonding that prevented radicals from undergoing condensation reactions with other biopolymers. This theory is based upon the fact that of the solvent parameters evaluated the Hansen solubility parameter for hydrogen bonding, δ_H, had the highest correlation with yield. These results provide a roadmap based on fundamental aspects of solvent structure that aim towards improving liquefaction yield, while also improving the quality of the polyol produced.

In chapter 6 bark-based polyols produced at 90 and 130 °C were contrasted to see how liquefaction temperature impacts foam properties, and both bark-based polyols were compared to control samples (no bark) to understand how the presence of bark-biopolymers impact foam properties. From analysis of the foaming behaviour it was found that the presence of liquefied bark-biopolymers was most influential in terms of their type of alcohols present and hydroxyl value. The presence of liquefied bark-biopolymers did manifest itself in the thermo-mechanical foam properties and the measurements of open-cell content. Bark-based PUFs (especially the sample produced at 90 °C) exhibited less intense tan δ peaks and no rubbery plateau in the storage modulus. This signified a rigid polymer, but with a less cohesive network formation. This may be attributed to a polyol with overall high functionality (provides rigidity), but that has the presence of some low functionality or very short molecular weight chains in the polyol (small chains have less potential for dampening). This may also explain the high open-cell content, since the presence of degradation compounds would have plasticized the highly fragile polymer membranes and led to their rupture. These results were supported by the optical micro-graphs that showed a less uniform foam structure and the soluble fraction values that indicated leachable compounds from the bark-based foams. Despite these results, the mechanical testing of the foams revealed that the foam produced from bark liquefied at 130 °C had comparable compressive strength to the PEG-G control foam. Based on the characterization of the polyol in chapter 4, the polyol produced at 130 °C had a molecular weight profile that enabled the formation of a more stable network with a higher degree of cohesiveness. These results show the promise of bark-based foams since they do not differ greatly in mechanical properties from control samples, and there yet remains avenues to improve their properties through optimization of the formulation.

In chapter 7 both bark and alkaline extracts of bark were alkoxylated to produce polyols, and a preliminary investigation of the mechanical properties was done. From the reaction behaviour it was found that the presence of acidic moieties in the alkaline extracts, despite their higher accessibility, retarded the reaction rate and conversion yield. However, the alkoxylation of the bark achieved a higher
yield than liquefaction. More importantly, a higher molecular weight polyol with less degradation was produced, but that had far better solubility due to the grafting of polypropylene oxide chains. The combination of a higher molecular weight, less degradation, and a higher biomass conversion yield, have all led to a polyurethane network that was superior to that made from a liquefied bark-based polyol. In chapter 5 it was shown that liquefactions in secondary alcohols led to greater amounts of degradation since they were not able to prevent condensation reactions. The work in chapter 7 has shown that alkoxylation was able to produce a polyol with secondary alcohols without the associated degradation that came with a liquefaction reaction. This was quite a promising result that was only achieved due to the detailed characterization of the polyol in the previous chapters that elucidated relationships between reaction conditions to the structure of the polyol, and ultimately to the properties of the foam.

List of Contributions

1. Chapter 4: The liquefaction of bark at three different temperatures yielded many new insights due to the in depth characterization of the polyol.

   (a) This work marks the first time a polyol was characterized using $^{31}$P-NMR. It revealed that liquefaction at lower temperatures preserved the secondary alcohols of some sugars. This is of importance since previously the total hydroxyl value was a prime characteristic; however this showed that the type of alcohols present must also be considered. As well it showed that liquefaction was able to completely convert all the phenolics into aliphatic alcohols, this is important since phenolics produce weak urethane linkages. Although this reaction of glycols condensing onto phenolics is well known, this work showed that the liquefaction conditions were conducive to complete conversion.

   (b) Few papers have provided molecular weight data on their polyols produced via liquefaction, and when data is provided it simply consists of a value for $M_w$ or $M_n$ without a chromatogram. The reason for this is that polyols produced via liquefaction tend to have very low solubility in common gel permeation chromatography solvents. This means that either the values reported are of the soluble fraction, and thus not representative of the whole polyol or GPC analysis is still performed but compounds are retained on the column and so the analysis is still not representative. In this work the polyol was benzoylated to improve both solubility and detection by a UV detector to facilitate its characterization. This revealed the true nature of the polyol, as a solution containing a very broad range of molecular weights. From the chromatograms of the polyols it is clear that $M_w$ or $M_n$ values are inadequate at representing distributions of molecular weight with multiple peaks and plateaus ranging up to 10,000 Da. The relatively flat plateau of distributions in P130, relative to P90 that had a large peak of low molecular weight compounds, played a crucial role in explaining the foam properties discussed in Chapter 6.

2. Chapter 5: The liquefaction of bark using various polyhydric alcohols and organic cosolvents helped provide key insights into the role of solvents on liquefaction yield, composition, and the extent of degradation.
(a) Few studies have investigated the effect of different solvents on liquefaction, and those that have focused on maximizing the conversion yield, without consideration for other factors like the extent of degradation or condensation. It was found that among polyhydric alcohol solvents, structures with a low equivalent weight and with primary alcohols were able to reduce the amount of acid insoluble lignin (AISL) formation (condensation side reactions). The highly polar primary hydroxyls and the short chain length resulted in a reaction environment that promoted condensation with the glycols over other biopolymers. This was based on the compositional analysis of the residues, elemental analysis of the residues, and $^1$H-NMR analysis of peaks corresponding to sugar degradation products.

(b) With regard to the organic cosolvents, it was found that ketonic solvents like acetyl acetone and cyclohexanone reduced AISL formation. From a correlation of literature solvent parameters to liquefaction yield it is likely that the ability of these solvents to donate electron density / accept protons, and thus engage in hydrogen bonding through their carbonyl group, played a crucial role in blocking condensation reactions with other biopolymers, and thus inhibiting AISL formation. These findings relating specific features of solvent structure to the extent of degradation and extent of condensation reactions is a significant contribution to the literature that was lacking more fundamental studies on the mechanisms underlying the liquefaction reaction.

3. Chapter 6: The liquefaction of bark at two different temperatures, and subsequent characterization of the foaming and the foam properties provided new insights into the effect of bark on foam properties.

(a) Studies using liquefied biomass-based polyols to make PUFs have focused on the mechanical properties. This work used a custom device to measure both the change in height and temperature throughout the foaming reaction. This clearly showed how liquefaction at a lower temperature preserved secondary alcohols that reacted slower compared to primary alcohols, and resulted in a longer time to reach the maximum height. This is of importance since this could reflect a slower rate of curing, and may explain the poorer morphology due to excessive cell coalescence.

(b) An important morphological feature of PUFs is the closed-cell content. Although rarely reported, it is important for understanding both the heat transfer behaviour and the elastic compressive behaviour of the foams. This work showed that both bark-based polyols had low closed-cell content. This is the first time this has been addressed in the literature. It is presumed to be due to the inclusion of low molecular weight/low functionality degradation compounds that plastisize the membrane or to the presence of anti-foaming agents (high surface energy species) that destabilize the membranes. These low closed-cell content values were manifested in the low elastic modulus of the bark foams. Therefore, by characterizing the closed cell content a strategy to improve the compressive behaviour of the foams has been identified. This is useful to other researchers in the field since it may be applicable to other types of biomass and may improve the quality of liquefied biomass-based PUFs.

4. Chapter 7: The alkoxylation of bark and the alkaline extractives of bark provided insights into how a different mechanism of converting bark could be used to improve polyol quality.
(a) Alkoxylation is known to be a polymerization reaction that produces a polyol through derivatization. It was unknown how applicable this approach would be to a lignocellulosic material like bark. As the first paper reporting the alkoxylation of bark it was found that the conversion yield was lower than other types of biomass due to the recalcitrant structure of the bark as well as the presence of acidic groups that retard reaction rate. However, the yield was still considerably higher than from liquefaction. The polyol characterization also showed that the polyols only contained aliphatic alcohols, mostly secondary alcohols, and the polyol had a very high molecular weight and broad plateau of molecular weight distributions, yet better solubility. These polyol qualities manifested themselves as an improvement in the compressive behaviour compared to that of the foams made from liquefaction. It should be noted that the foams made in this work were of a preliminary nature. There remains to be many areas of optimization from the foaming process to the formulation. This is of relevance to the field since alkoxylation has proven itself to be a conversion method that is easily adopted by industry and has demonstrated that bark is a promising material for making polyols and PUFs.

5. Technological and Industrial Relevance: This work developed a versatile method for the conversion of biomass into a polyol by exploring the variable space of both liquefaction and alkoxylation. It also performed the first alkoxylation of bark and showed that an industrially friendly method can be adapted to a feedstock like bark or bark extracts. Finally, this work focused on lodge pole pine, however the methods and results can be extended to that of other species as well as other types of biomass.

Concluding Statements

The work described herein has shown that improvements can be made to the quality of the polyol by understanding the conversion processes in greater depth and linking their reaction parameters to the structure of the polyol. Steps have been taken towards the demystification of the bark polyol’s structure, beginning the vital transition from a complex slurry of biomolecules towards a carefully crafted stew with known composition and predictable properties. For implementation in industry new questions must be addressed regarding the variability, reproducibility, stability, and economic viability. It is hoped that with future work on bark and other types of lignocellulosic biomass that these questions will be answered and these bio-polyols can be adopted by industry. Manufacturers of polyurethane products will enjoy the profitability while improving performance, the logging industry and sawmills will reap rewards from valorization of a waste product, and we as a society will continue to walk the path towards a renewable and sustainable future.
Chapter 9

Future Work

Exploring the cause of cell-membrane instability in bark-based PUFs

Cell-membranes are an important aspect of a foam since they dictate the heat transfer behaviour of the foam and play a role in the compressive behaviour. In the former, membranes prevent gas from flowing and thereby hinder the rate of heat transfer. In the latter, membrane stretching and gas-pressurization can increase the compressive modulus of the foam.

It was shown in chapter 6, that the foams from liquefied bark were mostly open-celled foams. In contrast the control PUFs were mostly closed-cell. This suggests that a component from the bark or a compound produced during the liquefaction makes cell membranes collapse. Papers in the literature rarely characterize the open-cell content of foams made from liquefied or alkoxylated polyols. Therefore, the cause of cell membrane collapse has not been discussed in the literature previously. There are two plausible contributors to cell membrane instability. The first is the presence of high surface energy compounds that act as anti-foaming agents. The second is the presence of compounds that have low functionality or no functionality. These compounds can act as a plasticizer that allows polymer to drain from the membrane during curing, resulting in thin, fragile membranes.

To address this issue, the polyol will undergo the following solvent extractions: diethylether to extract non-polar compounds without hydroxyl functionality; triethylamine to extract polar compounds without hydroxyl functionality; isopropyl alcohol to extract polar compounds with hydroxyl functionality, but that cause high surface tension. These distinctions are likely to be blurred, but should ultimately be able to extract a variety of small molecular compounds that may be responsible for membrane instability.

The polyols will then be used to make a foam and the open-cell content will be measured to see if a change is observed. If there is an improvement, the solvent from the extraction could then be characterized via H-NMR and C-NMR to determine the compounds that were responsible. If the open-cell content is reduced, then the PUF’s heat transfer behaviour and compressive behaviour can be evaluated to see if there is an improvement. Furthermore, this information will prove useful to other researchers evaluating the liquefaction and alkoxylation of other types of biomass since it may improve the characteristics of their polyol.
A method for the determination of the functionality of biomass-based polyols

At this stage the polyols have shown great promise; however to be useful to industry they must be able to be incorporated into a polyurethane formulation and have predictable properties. To achieve this the functionality of the polyol must be known. Functionality is the number of hydroxyl groups per molecule. This will dictate the cross-linking density and glass transition temperature of the PU polymer. Both of these structural characteristics are important for understanding material properties like the compressive strength. Synthetic polyols have well defined functionality, e.g. glycerol is 3, PPG/PEG is 2. However, bio-polyols produced from liquefaction or alkoxylation have a range of functionalities due to the diversity of both structure and molecular weight. The literature has rarely discussed this matter, and if so indirectly through determination of the PUF’s cross-linking density and glass transition temperature.

To address this issue a series of PU films will be made, using synthetic polyols of known functionality and equivalent weight (the molecular weight divided by the number of hydroxyl groups in the molecule). The cross-linking density of these films can be determined through solvent swelling measurements. Multiple linear regression can then be used to come up with an equation relating cross-link density to functionality and equivalent weight. This will determine $\alpha$ and $\beta$ values since the functionality and equivalent weight are known for these polyols.

$$\rho_{cd} = \alpha X_{fn} + \beta X_{eq.wt} \quad (9.1)$$

$$X_{eq.wt} = \frac{M_n}{X_{fn}} \quad (9.2)$$

$$\alpha X_{fn}^2 + \rho_{cd} X_{fn} + \beta M_n = 0 \quad (9.3)$$

The cross-linking density of the bark PU films can be determined using the method mentioned above. The equivalent weight is unknown for bark polyols; however it is equal to molecular weight divided by the functionality. The GPC molecular weight data can be substituted and now an estimation can be made for the functionality.

Since functionality is a key characteristic of a polyol it would enable researchers to make better comparisons. For example, future studies could look at how species, type of biomass, conversion process, reaction conditions vary the functionality. These factors have been alluded to previously by measuring glass transition temperatures or compression strength, but functionality would serve as a simpler and more instructive metric upon which to compare.

The optimization of the foaming process and formulation

The foams produced in this work were made in open containers using a typical foam formulation for rigid foams. Although this provided a good basis for exploration, there remains much that could be addressed and used to improve the properties of the foams, mainly to do with the formulation and foaming process.

Regarding the formulation the use of surfactants, a different blowing agent than water, and the
blending of an additional polyol, could have the largest impact on improving foam properties. The foams described in Chapter 6 were described to have a low closed cell content. It may be possible that the components within a biomass based foam require special surfactants. Therefore exploring the use of different surfactants may greatly improve their ability to insulate and also provide an improvement to the compressive behaviour. Also, water as a blowing agent is convenient, but is rarely the sole blowing agent. This is because it consumes lots of isocyanate and produces lots of small urea linkages that can greatly increase the brittleness of the foams. Therefore, by using an alkane or a halogenated hydrocarbon blowing agent would be an additional avenue to improve foam properties if the closed-cell content could be improved to retain the gas. Finally, few foam formulations consist of a single polyol, but rather a blend. Since some biomass-based polyols have a very high viscosity they may exhibit poor mixing during the foaming process that translates into a heterogeneous and weak foam. However when blended with even a small amount of a low viscosity polyol, the foam can be vastly improved.

Regarding the foaming process, the strategies that could be employed to improve the foam properties are improving the mixing of the foams, controlling the density, and controlling the temperature. Additional work on the initial curing behaviour of the foams, i.e. determination of the cream and gel time, would help ensure that mixing was done for as long as possible without shearing the newly formed polymer, and perhaps a higher RPMs can be used for mixing. Controlling the density of the foams can play an important role in improving the isotropic behaviour of the foams. When foamed in an open mould the cell will elongate along the rise direction, making the foams stronger in the rise direction, and weaker in the transverse direction. By having a closed cell mould the foam cell will be equiaxed and will provide a truer representation of the foam behaviour. Finally, controlling the temperature of the foams may improve the foam properties. Through the use of a heated mould it would allow the foams to fully cure by providing thermal energy to chains, ensuring that vitrification does not occur. Furthermore, this would facilitate a better comparison between samples since the type of alcohols present in the polyol would no longer influence the foaming as strongly.

These additional steps towards optimization and increased understanding of the formulation and foaming process that the bark-based foams can be evaluated in a more judicious manner and will help with the transition from research to development for various applications.
10.1 Data Table of Specific Compression Strengths of Literature Foams

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