COMPARATIVE ANALYSIS OF DIFFERENT LIGNINS AS PARTIAL POLYOL REPLACEMENT IN POLYURETHANE FLEXIBLE FOAM FORMULATIONS

By

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ABSTRACT

COMPARATIVE ANALYSIS OF DIFFERENT LIGNINS AS PARTIAL POLYOL REPLACEMENT IN POLYURETHANE FLEXIBLE FOAM FORMULATIONS

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Polyurethane (PU) foam consumers and producers are actively looking for ways to improve the sustainability of their products by replacing petroleum-based raw materials with biobased, sustainable raw materials. Lignin contains both aliphatic and aromatic hydroxyl groups, making it a suitable natural polymer to replace petroleum-based polyol in the formulation of polyurethanes. Previous studies have shown that the incorporation of lignin in PU foams increased flame retardancy, antimicrobial, and mechanical properties of the foams such as compressive strength and Young's modulus. This study is focused on evaluating the suitability of a wide range of lignins isolated from different plant sources and chemical processes in replacing 20 wt% of petroleum-based polyol in the formulation of PU flexible foams. The main emphasis was to study the effect of lignin incorporation on the foam's structural, mechanical, and thermal properties. The results showed that incorporating 20 wt% lignin increased tensile, compression, tear propagation strengths, and support factor of the developed PU flexible foams. Additionally, statistical analysis showed that foam properties such as density and compression force deflection were positively correlated to lignin's total hydroxyl content. In contrast, ultimate elongation was negatively correlated with the lignin's total hydroxyl content. Among tested lignins, organosolv lignins were the most suitable lignins for partial replacement of polyol in PU flexible foams designed for automotive applications, because they had higher solubility in co-polyol, lower glass transition temperature (T_g) and lower hydroxyl content compared to kraft lignins.

Dedicated to my parents
Madhav and Kapila Gondaliya

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

1.1.1 Polyurethane

Polyurethanes (PUs) are versatile polymers and can be manufactured in a wide range of densities, morphologies, and stiffnesses, which enable them to be commonly used in various thermosetting and thermoplastic applications such as coatings, adhesives, foams, elastomers, and fibers [1]. In 1937, Otto Bayer [2] synthesized the first polyurethane through the primary diisocyanate polyaddition reaction with a polyester diol. Previously, only polyester polyols were used to manufacture polyurethane; since the introduction of polyether polyols in 1957, polyurethane usage has increased significantly [3]–[5].

Polyurethane consists of blocks of copolymers with soft and hard domains (Figure 1) [3]. Soft domains are long, flexible, and stretchable chains, usually polyols (e.g., polyester or polyether oligomers), to make the foam more elastic [3]. Hard domains consist of relatively rigid segments, often isocyanates in foams (e.g., aromatic polyurethane-polyurea segments), which physically crosslink with the soft domains and make the polymer stiff [3]. Therefore, polyurethane products can be manufactured for a specific application by changing the ratio and composition of these soft and hard blocks. For example, mattresses, furniture cushioning, automotive, and household seating are manufactured using flexible polyurethane foams.

The global polyurethane market was valued at USD 95.13 bn in 2019 and is projected to grow at a compound annual growth rate (CAGR) of 12% during the forecast period from 2019-2023 to reach USD 149.91 bn [6].

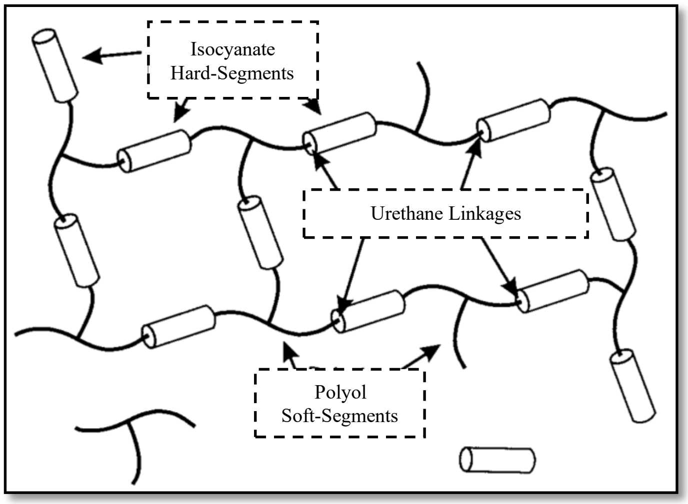


Figure 1: Crosslinking in polyurethane polymers [3]

Polyurethane polymers are manufactured from the commodity chemicals, such as polyisocyanates, polyesters polyols, and polyether polyols [4]. The common aspect of polyurethane products is the formation of urethane linkage (–NH–(C=O)–O–) during the polyaddition reaction (Figure 2) of polyol (molecules with two or more hydroxyl (–OH) functional groups) with molecules containing di- or poly-isocyanate (–N=C=O) group [7], [8].

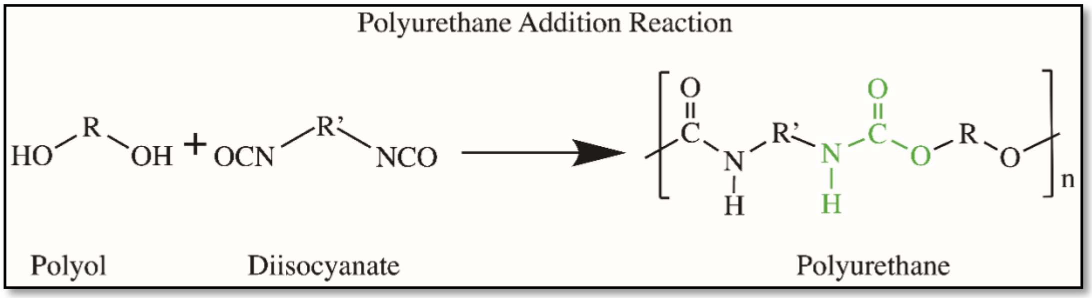


Figure 2: Polyurethane addition reaction

1.1.2 Polyol

The polyol is one of the main components of the polyurethane formulation with weight fraction ranging from 30 – 70 wt%, depending on the application as given in (Table 1) [4]. The global polyol market was valued at USD 12.44 bn in 2017 and was projected to grow at a CAGR of 9% during the forecast period 2018-2022 [9].

Table 1: Weight fraction of polyol in various application[4]

Applications	wt % of the polyol in the formulation
Flexible foams	70 %
Rigid insulation foams	30 %

Polyols with high molecular weight chains and lower hydroxyl values (OH functionality) acts as a soft segment in the final polyurethane polymer, providing softness and flexibility [4]. On the contrary, low molecular weight polyol with high OH values (around 3-8 hydroxyl groups/molecule), tend to give a more crosslinked, semi-rigid / rigid polymer. Rigidity and high crosslinking density occur due to the formation of more urethane linkages of hydroxyl groups with isocyanate moieties. The structure and properties of the polyurethane products depend on the type, and the ratio of polyol, di- / poly- isocyanate, other additives, as well as the synthesis route used [8].

1.1.3 Flexible Polyurethane Foam

Polyurethane foams are among the most significant commercial products, commonly characterized as rigid, semi-rigid, or flexible foams, depending on their core densities, stiffness, and mechanical performances [1]. The main applications of PU foams range from the automotive industry, including seat cushions, bumpers, furniture industry, upholstery, insulation, construction, packaging, and medical devices [5]. According to the global forecast reports, the PU foams market was valued at USD 50.21 billion in 2017 and is projected to reach USD 79.77 billion by 2023, growing at 8% CAGR during the period 2017-2023 [10]. In 2019, flexible foam products (Figure 3) accounted for almost 46.4% of the total PU foam industry revenue [11].

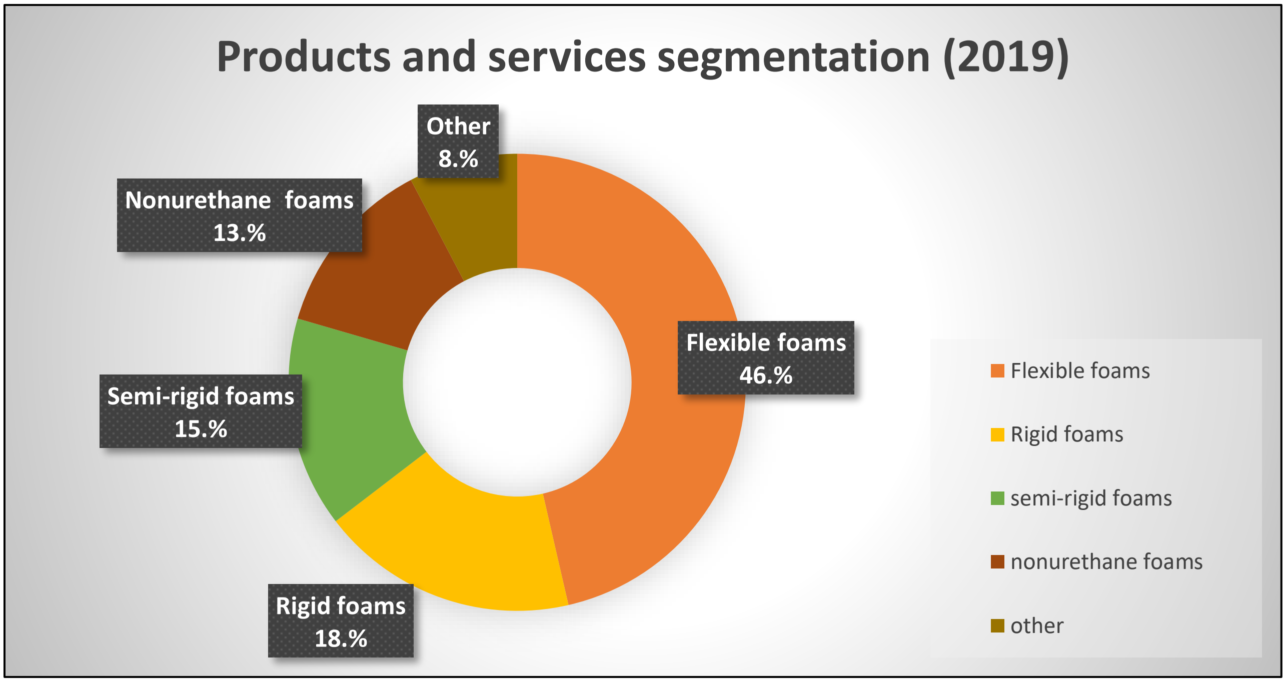


Figure 3: Products and services segmentation for polyurethane products (Pie chart recreated from IBIS world report [11])

1.1.4 Flexible PU Foam Chemistry

Polyurethane flexible foam, as shown in (Figure 4) is formed by the simultaneous occurrence of a polymerization reaction and a blowing reaction. The polymerization reaction comprises the reaction between the hydroxyl group within a polyol (polyether or polyester-based polyol) with an isocyanate group to form a urethane linkage. Polyol with a high molecular weight and lower OH (hydroxyl) functionality (2-3 hydroxyl group/molecule) are generally used in polyurethane flexible foam formulations.

The blowing reaction can occur with a physical or chemical blowing agent [1], [3]. Physical blowing reagents are the ones that do not take part in the chemical reactions (e.g., pentane, hydrochlorofluorocarbons, chlorofluorocarbons, perfluorocarbons, fluorinated ethers, liquid carbon dioxide, and fluorocarbons) [3], [5]. These physical blowing agents have a low boiling point and hence get converted into the gaseous state by the exothermic heat, liberated during the polymerization reaction in the foam formulation. On the contrary, chemical blowing agents such as water participate in the reaction to release a gas, which facilitates the foaming process; for example, carbon dioxide gas is generated by the reaction of water and isocyanate, as shown in (Figure 4) [5]. This carbon dioxide gas then expands to form a cellular network in the foam. In addition to the evolution of carbon dioxide, the blowing reaction also produces heat and substituted polyurea [3]. The polyurea acts as the hard segment in the final polymer by providing hydrogen bonding sites between the NH-groups of urea and urethane linkages with the lone pairs of carbonyl oxygen atoms of polyester or polyether chains [12]. The rate of polymerization and the rate of carbon dioxide gas formation from the reaction of water and isocyanate can be balanced either by ensuring the polyol and isocyanate have appropriate reactivities or by using various additives like gelling catalyst, blowing catalyst and surfactants [3], [5].

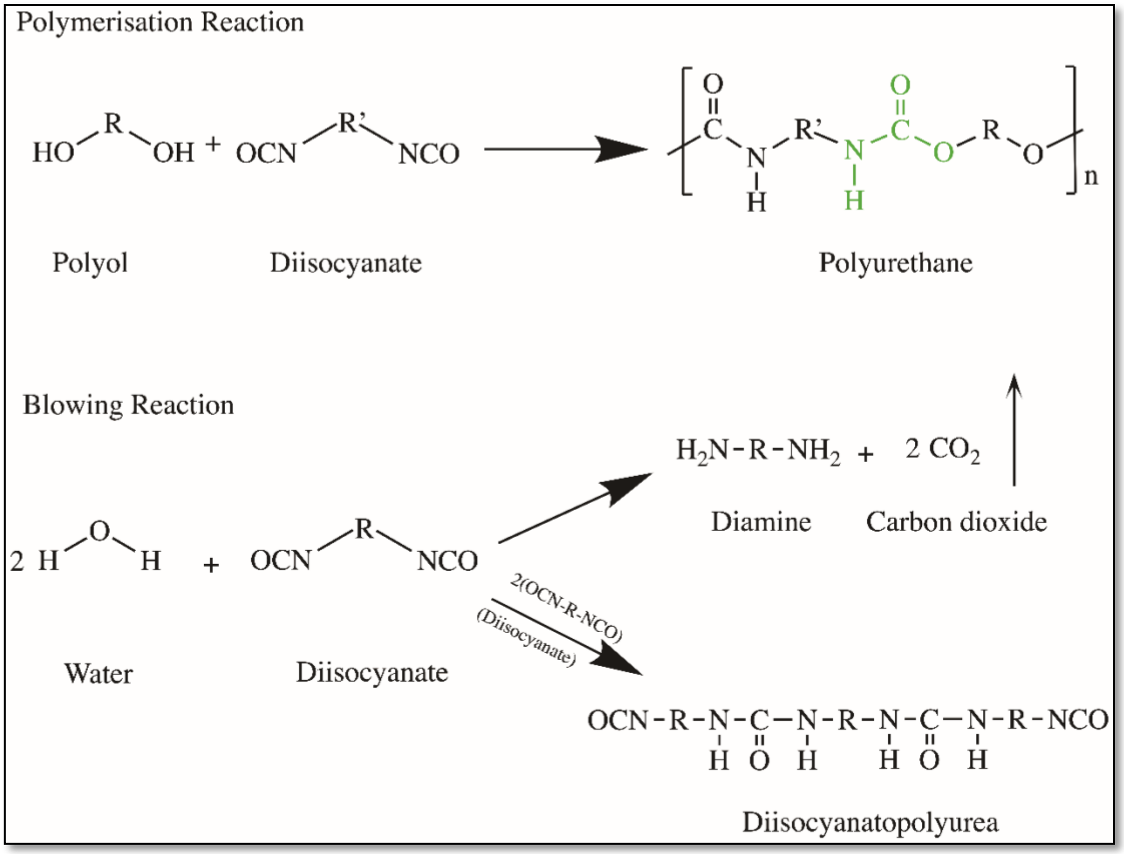


Figure 4: Flexible foam reaction mechanisms

1.1.5 Lignin

In 1838, when Payen [13] treated wood with concentrated nitric acid, some portion of the substance was dissolved, and a solid fibrous residue, termed ‘cellulose,’ was left. The dissolved part had a higher carbon content than that of the fibrous residue, which was termed ‘lignin’. De Candolle [13] first introduced the term ‘lignin’ in 1819, derived from Latin word for wood, ‘lignum’. Lignin is one of the main components of the cell walls of plants and is an enormous potential resource for use in renewable polymers. In addition to polysaccharide cellulose and hemicellulose, lignin is one of the major structural biopolymers in plant cell walls. Lignin can contain up to 15-30% of the plant’s mass on a dry basis [14]. The properties and structure of the lignin in a plant before any chemical processing depends on its source derived from plant taxonomy and genotype, tissue type, environment, and development stage [15].

The structure of lignin differs considerably among plant species due to the variation in the proportion, type, and linkages among the monomers that exist in the lignin molecule. These monomers are called monolignols [16]. The monolignols consist of phenylpropane, the basic structural unit of lignin, with different degrees of substitution by methoxyl groups on the aromatic ring (Figure 5).

1.1.5.1 Lignin Sources

Softwood lignins are mainly composed of coniferyl alcohol; on the other hand, hardwood lignins consist of both coniferyl and synapyl alcohol, and grass lignins/annual crops contain all the three types of monomers (coniferyl, synapyl, and p-coumaryl) [17]. The proportion of the three monolignols in lignin determines the type of inter-unit linkages present in the lignin macromolecule, which defines the degree of branching [18], and the reactivity of lignin [19]. In general, the diversity in inter-unit linkages is a consequence of a high degree of heterogeneity in the molecule, as visualized in (Figure 6).

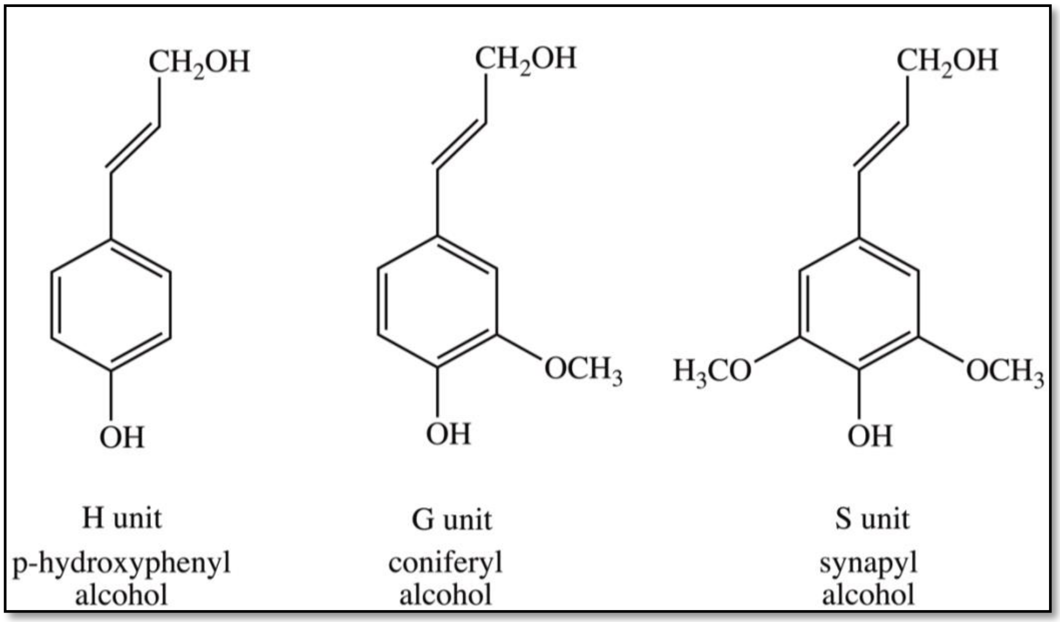


Figure 5: The three prominent monolignols, with associated nomenclature of C atom [20]

The lignin molecule carries various functional groups, predominantly aliphatic and aromatic hydroxyl groups, [13], [16], but lignins can also contain carbonyl or carboxyl functional groups. Despite intensive studies, the data available for the composition of functional groups cannot be summarized simply due to significant variations among the wood species. (Table 2) shows an idea of the frequencies of functional groups in lignin [13].

Table 2: Functional groups of hardwood and softwood lignin (per 100 C_6C_3 Units); [13]

Functional Groups	Softwood Lignin (per 100 C_6C_3 Units)	Hardwood Lignin (per 100 C_6C_3 Units)
Methoxy	92 – 97	139 – 158
Phenolic hydroxyl	15 – 30	10 – 15
Benzyl alcohol	30 – 40	40 – 50
Carbonyl	10 – 15	---

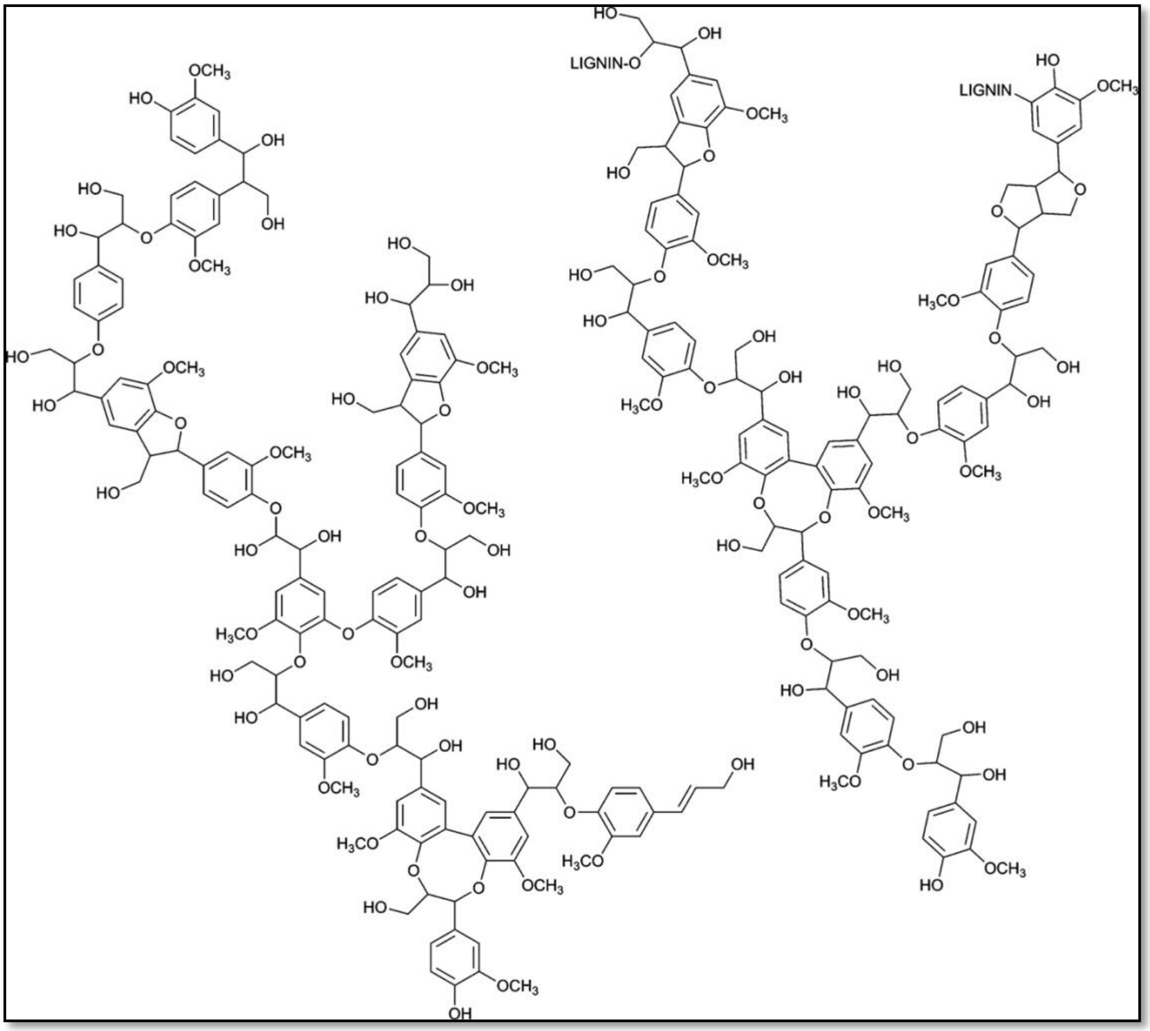


Figure 6: Structure of softwood lignin, image reproduced from [21]

1.1.5.2 Lignin Extraction Processes

There are different types of lignin, whose characteristic structures and chemical properties depend on the delignification treatment and types of biomass [20]. Lignin samples used in my research are mainly from three processes: kraft, sulfite, and organosolv processes, which are explained in detail in the following section.

1.1.5.2.1 Kraft Lignin

Kraft lignin is produced by the sulfate (kraft) cooking process. It comprises about 85% of the world's total lignin production [22], with an annual output of around 63×10^4 tons. A significant proportion of kraft lignin is used only in low-value applications such as the generation of process steam and energy by incineration [23]. During the kraft process, around 90 to 95% of the lignin confined in the wood is dissolved into an aqueous solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) [24]. Lignin breaks down into smaller molecular weight fragments during the cooking process, which are soluble in an aqueous solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) [24]. Kraft lignin contains a significant amount of phenolic hydroxyl groups because of the extensive breakage of β-aryl bonds during the cooking process [24]. Kraft lignin has an ash content of around 1 to 5 wt% [25], molecular weight ranging from 200 to 200,000 g/mole [26].

1.1.5.2.2 Organosolv Lignin

Organosolv pulping processes use a mixture of organic solvents as a cooking medium to solubilize lignin and hemicellulose [27]. The commercial solvents are formic acid, ethanol, acetic acid, and peroxy acid [28], [29]. n organosolv pulping processes, lignin is extracted via solubilization, resulting in more homogeneous lignin with less chemical modification than lignins isolated through kraft and soda processes [30]. Organosolv lignin features the following characteristics: low molecular weight, high purity, hydrophobicity, and high solubility in organic solvents [31].

1.1.5.2.3 Lignin from Sulfite Process

Lignosulfonate lignin is obtained as a byproduct of sulfite cooking, in which HSO_3^- and SO_3^{2-} ions are used for the delignification of wood [32], [33]. Lignin is sulfonated, solubilized, and degraded during the process. Lignosulfonate lignin comprises a variety of functional groups: carboxylic groups, phenolic hydroxyl groups, and sulfur-containing groups, e.g. ($-SO_3^-$) [34]. Chemical properties and structural characteristics of lignosulfonate lignin are high molecular weights, high polydispersity index, high solubility in water, and having quite high ash content (around 4-8 wt%) compared to kraft and organosolv lignins [31].

1.1.6 Motivation to Replace Petroleum-Based Polyol

Flexible polyurethane foams are synthesized via a polyaddition reaction between di- or poly-isocyanates with polyols in the presence of other additives to adjust the foam properties [4]. However, most of these chemicals are derived from petrochemicals, so the volatility of crude oil prices results in the fluctuation of the cost of polyurethane products. Moreover, depending on high-volume fossil fuel chemicals for polyurethane products has raised serious environmental concerns. Also, the advancement of society's interests toward more sustainable products and technologies has motivated researchers and industries to look for renewable feedstocks [7], [35]. The use of green polyols is likely to increase, indicating an enormous opportunity for growth in biobased polyols usage [14].

A number of other renewable raw materials have been used as polyol replacement in the synthesis of PU foams, such as vegetable oils like palm oil [36], [37], rapeseed oil [38], sunflower oil [39], soybean oil [40] and castor oil [41]. However, there are some challenges in using vegetable oils for PU flexible foam formulations. For instance, vegetable oils have unsaturated double bonds, which need to be converted to hydroxyl groups through series of initial steps such as epoxidation, hydroformylation, and reduction/ozonolysis, which can increase the production cost and time [42]. Other biobased polyols derived from industrial byproducts such as wood-based polyols [43], [44], and bio-pitch (generated during Eucalyptus charcoal production) [45] have also been studied for the production of sustainable and eco-friendly polyurethane flexible foams. The foams produced using biopitch had very high density in the range of 100-160 kg/m$_3$ and were less thermally stable compared to petroleum-based flexible PU foams [45].

Among these naturally occurring raw materials, lignin is a promising candidate for producing biobased polyurethanes, because of its abundant availability in nature. Moreover, it comprises complex chemical structures with aliphatic and phenolic hydroxyl groups, which can react with the isocyanate to produce urethane linkages [46]–[48]. It was reported in 2015, that the worldwide lignin production is approximately 100 million tons annually. In the year 2017, nearly140 million tons of lignin was generated just by paper and pulp industries annually as the main byproduct [49]. Most of these lignins are used as a source of fuel to generate power for the plants [50], [51]. Lignin obtained from industries (paper, pulp, and biorefineries) provides excellent mechanical properties to the PU foam due to its aromatic structures [52]–[54]. Lignin samples extracted from biorefining processes and various chemical pulping processes such as kraft [50], [55]–[58], soda [7], [59], sulfite [60] have been studied to replace polyol in polyurethane flexible foam synthesis. Studies have shown that lignin incorporation not only increases the biobased content of the polyurethane products but also provides better performance advantages, such as ultraviolet (UV) stability [61], mechanical strength [50], fire retardancy [62], [63], biodegradability [64], and antioxidant [61] properties to the final PU foam.

1.1.7 Challenges in Lignin Utilization

Lignin has a complex structure, as shown in (Figure 6); therefore, the accessibility of hydroxyl functional groups present in lignin to react with an isocyanate group is obstructed because of the steric hindrance, which results in lower lignin reactivity [65]. Besides that, within the lignin polymer itself, there are different kinds of hydroxyl groups, such as primary and secondary aliphatic, carboxylic, and phenolic hydroxyl groups. The reactivity of the alcohol (OH group) with isocyanate groups for the formation of urethane linkages can be ranked in the following order: primary (1°) > carboxylic (-COOH) > secondary (2°) ≫ phenolic (Ph) hydroxyl groups [66]. It was reported that the reactivity rate of a primary alcohol with an isocyanate group in an uncatalyzed reaction is 1000-fold faster compared with the phenolic hydroxyl group, which results in the heterogeneity of the final product due to different reaction rates with an isocyanate [66].

Another barrier to the utilization of lignin in the development of flexible polyurethane foam is the high glass transition (T_g) temperature of lignin. Glass transition temperature of a material is a temperature at which a polymer changes from a hard and brittle state (glassy) to a soft and flexible state (rubbery). Typically, the T_g of lignin ranges between 90 °C –180 °C [67]–[71], whereas the glass transition temperature of PU flexible foam is below 0°C [72]. The polyols (soft segment in the flexible PU foam) provide flexibility and softness while the isocyanates and low molecular weight chain extenders provide hardness and stiffness to the resulting polymer [4]. Therefore replacing the soft segment with lignin, which has high T_g values, increases the brittleness of the polyurethane flexible foam [73].

Lignin also has a high polydispersity index (PDI). In polymer chemistry, PDI usually refers to the ratio of (average molecular weight-M_w) to the (number average molecular weight-M_n). PDI is a measure of the distribution of molecular weights of polymer chains in a given polymer. Lignin is polydisperse in nature, which means that it has a broad distribution of molecular chain lengths. Hence, the final PU flexible foam morphology will be heterogenous as smaller chains react faster than longer chains, and the ratio could be possibly different from batch to batch [74].

Lignin solubility in the co-polyol, used in the synthesis of polyurethane foam, is also a challenge [74], because lignin isolated through kraft, soda, and sulfite processes all have low solubility in most organic solvents [74].

Lignin has a dark brown color. The dark color of lignin comes from its chemical structure and chromophores, which are the light-absorbing groups and its chemical structure [74]. The dark color of lignin could limit its application in areas where aesthetic appearance is essential [74]. However, for the polyurethane flexible foam application, the color should not be an issue, because they are mainly fabricated and covered in cushioning applications.

Usually, lignins with high sulfur content such as lignosulfonate or lignin subjected to sulfuric acid pretreatment, have unpleasant odors [74]. It is economically challenging to get rid of the sulfur; therefore, lignin with low sulfur content, especially from biorefinery, low-sulfur kraft lignin, or organosolv lignins, are more suitable for polyurethane flexible foam applications [74].

1.1.8 Lignin-Based Polyurethane Flexible Foam

Lignin can be used either as fillers [75]–[77] or as a crosslinking reagent by reacting with isocyanate [58]. However, 100% substitution of the polyol with lignin in flexible PU foam is still a challenge due to the aromatic nature of the lignin, high T_g, and high hydroxyl value. The PU foam composed of 100 wt% lignin substitution (polyol component is wholly replaced with lignin) will potentially be brittle. Hence, a soft segment polyol is used to enhance the ductility of the lignin-based polyurethane foams [78].

There are very few research publications using lignin as a polyol precursor for the formulation of flexible polyurethane foams, summarized in (Table 3)

Table 3: Summary of previously published papers on lignin-based flexible PU foam

Author	Year	Lignin	Max Lignin Incorporation (wt% of polyol) *	Note
Jeong et al.[58]	2013	Kraft softwood	30	Dissolved unmodified lignin in PEG, using heat
Bernardini et al. [7]	2014	Soda lignin from non-woody biomass	25.8	Liquefied oxypropylated soda lignin via microwave treatment
Cinelli et al. [35]	2013	Kraft softwood	22.5	Liquefied kraft lignin via microwave treatment
Wang et al. [50]	2019	Kraft softwood	22.5**	Modified by grafting PEG2000 on lignin; Requires additional chemicals and energy intensive.
Wysocka et al.[60]	2016	Lignosulfonate softwood	20	Used unmodified lignin to get semi-rigid and rigid foams
Bernardini et al. [59]	2015	Soda lignin from non-woody biomass	20	Liquefied lignin via microwave treatment
Carrico et al.[55]	2016	Kraft hardwood lignin (Eucalyptus)	17.5	Synthesized semi-rigid foams
Gómez-Fernández et al.[56]	2017	Kraft lignin	10**	Functionalized lignin using isophorone diisocyanate (IPDI)

*Lignin wt% of the total polyol

** Modified lignin weight percentage means original lignin content in the polyol mixture will be lower

1.1.8.1 Unmodified Lignin as Polyol Replacement

Physical mixing is a simple method of homogenization of miscible raw materials [55]. Physical mixing of lignin is desirable without any physical or chemical pretreatment for direct use in polyurethane foam synthesis [55]. Moreover, PU foam manufacturers have shown great interest in using unmodified lignin because it reduces the overall number of steps in manufacturing a product, thus improving the overall process [55].

Carrico et al. [55] developed semi-rigid foams by using a biobased polyol mixture from industrial byproducts such as eucalyptus kraft lignin, crude glycerol, and castor oil using one-pot synthesis. These polyols mixtures were used to synthesize different polyurethane foam formulations with unmodified lignin contents ranging from 10-40 wt%; it was found that the synthesized foam with 17.5 wt% of unmodified lignin replacement showed better dimensional and thermal properties, as well as the best cell homogeneity compared to foam formulation with higher lignin content (20, 25, 30 and 40 wt%) [55].

Similarly, Jeong et al. [58] used kraft softwood lignin combined with polyethylene glycol as a soft segment for the PU flexible foam formulation. The maximum lignin loading achieved was 30 wt% of the total polyol mixture. It was reported that unmodified kraft softwood lignin was highly soluble in the polyethylene glycol, and no additional solvents or catalysts were required in the foam preparation [58]. However, the process used by Jeong et al. [58] used a higher temperature to dissolve lignin in polyol before adding that to the foam formulation.

Wysocka et al. [79] reported that they successfully synthesized rigid, semi-rigid, and flexible foams using lignosulfonate and hydrolyzed lignosulfonate lignin. The formulation had the lignin loading of 20, and 30 wt% of the total polyol used in the formulation. However, the produced foams had high glass transition temperatures (36-100 °C) [79].

Overall, a general trend was observed regarding density and compressive strength. As the lignin content increases, the density and the compressive strength increase [55], [58]. This trendwas due to the increase in the crosslinking density of polyol and isocyanate in the PU flexible foam formulations [80]–[82].

The synthesis of flexible foam requires polyol with low functionality and low viscosity [80]. Microwave treatment was investigated to obtain liquid polyols with shorter reaction time [84]–[86] using various lignins such as kraft [87] and soda [7], [59]. In a study published by Cinelli et al. [87], kraft lignin was added to liquefying polyols (glycerol and polyethylene glycol 400). The microwave treatment was used to obtain liquefied lignin, which was added to the other components of the foam formulations, such as chain extender, surfactant, blowing agent, and catalysts. Bernardini et al. [59] also used microwave treatment to liquefy soda lignin using glycerin polyglycidyl ether (EJ 300) and glycerol as the liquefying solvents. It was reported that foams produced with 12 wt% polyol replacement with liquefied soda lignin had mechanical and chemical properties comparable to those produced using pure petroleum-based polyols [59]. In another study, Bernardini et al. [7] reported that soda lignin after oxypropylation exhibited easier dissolution in co-polyols (glycerol and polyethylene glycol-400) and better miscibility with chain extenders (polypropylene glycol triol and castor oil). Whereby, the formulated foams using liquefied oxypropylated soda lignin had similar properties compared to foams made with liquefied soda lignin [7]. All the foams formulated using liquefied soda lignin (25.8 wt% substitution) had high open cell content, and thermal and mechanical properties which were ideal for applications in the interior part of car seats and packaging [7], [59].

The addition of lignin can be a challenge because of the steric hindrance caused by methoxy groups that make some of the hydroxyl groups less accessible [88]. Wang et al. [50] grafted long polyethylene glycol (PEG 2000) chains onto kraft lignin to improve the flexibility of developed foams compared to the unmodified kraft lignin. Wang et al. [50] reported that even after substituting 50 wt% of the polyol with the modified lignin, the elastic recovery of the foam was higher than 93% [50]. The studies listed in (Table 3) indicated that lignin can be used directly or after chemical modification into PU flexible foams via different methods such as hydrolysis [60], oxypropylation [7], or after liquefication [7], [57], [59]. Most of these lignin-based polyols production methods require the use of energy such as heat or microwave, to homogenize the phases and adjust the physical properties of polyol. The current research is the first study that focused on comparing the effects of various lignin properties on the final polyurethane flexible foam performance.

Using lignin (as it is) without any modification (oxypropylation, grafting, hydrolysis) or pretreatments (heat, microwave treatment) will improve the economic aspects of using renewable raw materials to replace petrochemicals, and reduces the use of solvents and energy-intensive processes [7]. Moreover, to increase lignin substitution, it is crucial to understand how the intrinsic properties of unmodified lignin extracted from various processes (kraft, organosolv, soda, and sulfite) affect the final PU foam performance. To the best of our knowledge, the maximum replacement of polyol to synthesize flexible PU foam with unmodified kraft lignin without any thermal or chemical treatment was just 17.5 wt% [55], and with unmodified lignosulfonate lignin, the polyol replacement was about only 20 wt % [60].

1.2 OBJECTIVES

The primary objective of this study was to evaluate the suitability of a wide range of unmodified lignins to partially replace petroleum-based polyol in PU flexible foam formulations. To achieve the first objective, flexible PU foam was developed using ‘one-pot’ synthesis by replacing 20 wt% of the petroleum-based polyol with lignin. Thirteen different unmodified lignin samples derived from different extraction processes (kraft, sulfite, and organosolv) and plant sources (softwood, hardwood, bagasse, peanut shell, and corn stover) were used.

The second objective was to study the effect of unmodified lignin incorporation on the structural, mechanical, and thermal properties of the foam to identify the most suitable lignins for the PU flexible foam application.

1.3 HYPOTHESIS

Based on previously published work and our knowledge of polyol used for PU flexible foam application, we believe that lignins with a low hydroxyl value (< 200 mgKOH/g), low molecular weight (< 5000-6000 Da), low glass transition temperature (< 150 °C), and low polydispersity index (< 2.5) would be more suitable lignins for the flexible PU foam formulations.

CHAPTER 2

MATERIALS AND METHODOLOGY

2.1 MATERIALS

2.1.1 Polyols

For the synthesis of flexible polyurethane foam, polyether-based polyol with OH number – 28 mgKOH/g was used.

2.1.2 Blowing Reagent

Distilled water was used as the chemical blowing agent for the synthesis of flexible polyurethane foam. The reaction of water with isocyanate is highly exothermic and produces an amine and carbon dioxide. The initial reaction product is a carbamic acid, which is highly unstable and further breaks down into primary amine and carbon dioxide, as shown in (Figure 7) [5]. The amine can react immediately with another isocyanate to form symmetric urea.

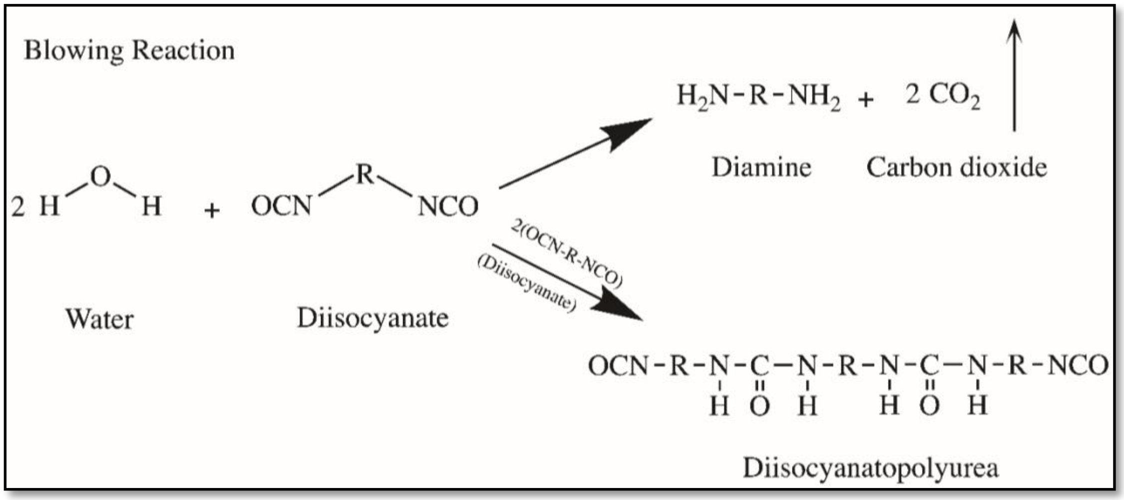


Figure 7: Blowing reaction between water and isocyanate

The blowing agent's selection depends on various factors, including the environmental considerations, toxicity, flammability, compatibility with the raw material, and the final product, safety, economic, and performance consideration [5].

2.1.3 Catalysts

Polyurethane foam formulation requires balancing two competing reactions, by adding complementary components such as catalysts to achieve the desired structure and properties of the final product [5]. Tertiary amines are used to catalyze the reaction between water (blowing agent) and isocyanate as well as isocyanate and polyol [5]. The catalyst controls the rate of both reactions. Amine catalyst is primarily considered to be a blowing catalyst because they tend to increase the rate of reaction between isocyanate and water. However, amines do catalyze both reactions, with relative reaction rates depending on the specific amine catalyst used [5].

2.1.4 Surfactants

The vast majority of surfactants used in the polyurethane flexible foam formulation are of the class called silicone surfactants [4]. The silicone-based surfactant used in this study helps stabilize foam structure, maintain cell regulation at low-use levels, and act as a cell opener to produce open-celled foam. In general, surfactants are considered to decrease the surface tension at polyurethane-air interfaces, which promotes the production of bubbles. Surfactants also act as emulsifiers to get a single-phase system and regulate the stability of the cell polymer surfaces [4].

2.1.5 Isocyanates

The isocyanate used for the synthesis of flexible polyurethane foam had % NCO (Isocyanate index) of 28. Therefore, the equivalent weight is calculated as 4200/%NCO, which will be around 150 g/mol.

Table 4: Properties of raw materials used in the flexible PU foam formulations

Raw materials	Functionality	Hydroxyl number	Equivalent weight
Polyol	-	28	2000
Water	2	6233	9.01
Gelling Catalyst	Not applicable	558	100.53
Blowing Catalyst	Not applicable	251	223.50
Surfactant	Not applicable	62	904.83
Diisocyanate	% NCO = 28	-	150

2.1.6 Commercial Lignins

Commercial lignin samples were purchased from or provided by lignin producers without further modification, as shown in (Table 5). Lignin samples for the formulation were characterized, and lignin properties such as hydroxyl value, glass transition temperature, polydispersity index, and molecular weight were measured. These commercial lignins had weight average molecular weight ranging between 3400-12000 g/mol, number average molecular weight ranging between 400-2250 g/mol; hydroxyl value ranging between 65-400 mgKOH/g; glass transition temperature ranging between 90-150 °C. Each lignin sample was used without further modification. Lignin was sieved using mesh No. 80 (180 μm) and then oven-dried at 105 °C for 1 hour before adding to the polyurethane foam formulation.

Table 5: Lignin used in the flexible PU foam formulations

Lignin #	Process	Source	Abbreviation	OH Value* (mg KOH/g)
1	Kraft	Softwood	1-K-SW	315
2	Organosolv	Hardwood	2-O-HW	256
3	Organosolv	Corn Stover	3-O-CS	219
4	Kraft	Softwood	4-K-SW	332
5	Organosolv	Peanut Shell	5-O-PS	191
6	Kraft	Softwood	6-K-SW	321
7	Kraft	Softwood	7-K-SW	301
8	Organosolv	Hardwood	8-O-HW	229
9	Lignosulfonate	Softwood	9-L-SW	65
10	Kraft	Softwood	10-K-SW	376
11	Kraft	Bagasse	11-K-BA	272
12	Kraft	Softwood	12-K-SW	360
13	Kraft	Softwood	13-K-SW	293

* OH Value was calculated based on ^{31}P-NMR data (**APPENDIX A**)

2.2 EXPERIMENTAL

2.2.1 Lignin Characterization.

2.2.1.1 Ash Content:

Five ceramic crucibles were oven-dried for 3 hours at 105°C and weighed to the nearest 0.1 mg. Lignin samples were loaded in each crucible, dried for 1h at 105°C to remove the moisture from the samples, and weighed. Samples were then transferred to a muffle furnace and heated with a 5°C/min ramp till 525°C and held for 4 hours. Percent Ash content was calculated and measured according to TAPPI T 211 om-02 standard method. The following equation (Equation 1) was used to determine ash content. Five replicates were run for each sample.

$$\%\ \text{Ash content} = \frac{W_{c+f} - W_c}{W_{c+L} - W_c} * 100 \qquad \text{Equation 1}$$

Where,

W_{c+f} : the weight of the dried crucible and lignin ash,

W_{c+L} : the weight of the dried crucible and dried lignin, and

W_c : the weight of the dried crucible.

2.2.1.2 Hydroxyl Content:

Hydroxyl content was measured using phosphorous nuclear magnetic resonance spectroscopy (^{31}P NMR). 40 mg of oven-dried lignin sample was dissolved in 300 µL DMF, 325 µL mixture of (anhydrous pyridine/deuterated chloroform) in the ratio (1.6:1, v/v), followed by the addition of 100 µL of cyclohexanol (22.01 mg/mL) as an internal standard. Then 50 µL of chromium (III) acetylacetonate solution (5.6 mg/mL) was used as relaxation reagent and 100 µL of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane as phosphitylation reagent. NMR analyses were performed on an Agilent DDR2 500 MHz NMR spectrometer equipped with 7600AS 96 sample auto-samplers, running VnmrJ 3.2A with a relaxation delay of 5s, pulse angle of 90°, and with 256 scans. Spectra were processed using MestreNova software (Mestrelab Research, Version 12.0.3).

2.2.1.3 Molecular Weight Analysis:

Molecular weight data (number-average molecular weight: M_n; weight-average molecular weight: M_w; and polydispersity index: PDI) of lignin samples were collected from acetylated lignin samples. A gel permeation chromatography system (GPC from Waters company with THF as mobile phase columns) was used for these measurements. Due to the inadequate solubility of some lignin samples in THF (tetrahydrofuran) solvent, it was first fully acetylated using a pyridine-acetic anhydride solution using the following procedure: 1g of lignin sample was added to 40 ml of pyridine-acetic anhydride solution (50-50 v/v%) [89]. The solution was mixed at room temperature for 24 hours (600 rpm). Then, 150 ml of hydrochloric acid with a pH of 1 was added to the solution to precipitate acetylated lignin particles. Precipitates were vacuum filtered, and residual solids were washed with hydrochloric acid (0.05 M) solution three times, followed by deionized water several times. A vacuum oven was used to dry acetylated lignin samples at 40 °C for 16 hours [90]. Next, the samples were dissolved in THF (HPLC grade) at a concentration of 5 mg/ml and were filtered using a syringe filter (PTFE, 0.45 μm); the filtrate samples were used for GPC analysis. A Waters GPC system (Waters e2695 Separation Module) was then used to analyze the filtrate at a flow rate of 1ml/min, using three 300 mm × 7.8 mm Waters columns in series including 1- Styragel HR 4 THF (5k-600kÅ), 2- Styragel HR 3 THF (500-30k Å) and 3- Ultrastyragel THF

(100-10k Å). Polystyrene standards of specific molecular weights (162, 370, 580, 945, 1440, 1920, 3090, 4730, 6320, 9590, 10400, 16200 Da) were used as calibration standards. The filtrate solution (25 µL) was injected into the system and was detected using a 2414 RI Detector, which was constantly maintained at the same temperature as the columns (35°C) during the analysis. Data were collected and analyzed using Empower GPC Software.

2.2.1.4 Elemental Analysis:

Elemental analysis for C, H, N contents were analyzed using a 2400 CHNS/O Series II System from PerkinElmer. For mineral contents, lignin samples were first digested using an open vessel microwave following the procedure provided in the SW846-3051A test method. After digestion, mineral contents were determined by Inductively Coupled Argon Plasma (ICAP) based on the method derived from AOAC 985.01 (American Association of Analytical Chemists).

2.2.1.5 Glass Transition Temperature:

A differential scanning calorimeter (DSC 6000, PerkinElmer) was used to determine the glass transition temperature (T_g) of all the lignin samples. Approximately 10 mg of lignin was weighed in a sealed hermetic aluminum pan and tested from room temperature (23 ± 2 °C) to 120 °C; at a heating rate of 20 °C/min for its first heating cycle and then cooled at a cooling rate of 20 °C/min to 25 °C and then kept isothermal for 10 mins. The second heating cycle was applied at a heating rate of 20 °C/min to 200 °C. All the cycles were run in the N_2 environment. The second heating cycle was used to determine the glass transition temperature (T_g).

2.2.2 **Synthesis of Lignin-Based Flexible Polyurethane Foams**

Lignin-based polyurethane flexible foam is synthesized using a reaction between two components, Part A and Part B, where Part A component comprises of diisocyante, and Part B comprises polyol and additives mixture.

Part B components: polyol was added in a 12 oz cup followed by the sequential addition of water, gelation catalyst, blowing catalyst, and silicone-based surfactant. The mixture was stirred at 2000 rpm for 30 seconds to ensure complete mixing. Then lignin was added in a particular percentage (equivalent to 20 wt% of total polyol), and the mixture was remixed again for 2 minutes at 2000 rpm to complete mixing.

Part A comprises of isocyanate, which was weighed accurately in a separate cup using a weighing scale with ± 0.1 mg least count and was added to component A; the mixture was then mixed vigorously at 2000 rpm for 4-5 seconds. Next, the mixture was immediately poured into the silicone molds (Figure 8), to rise in free expansion at 60 °C for an hour and then air-dried at room temperature for 24 h to ensure complete curing before characterization was done. The foams from the mold were removed and were cut accordingly for ASTM D 3574 test method.

Thirteen lignins were employed using the same formulation given in (Table 5) where 20 wt% of the total polyol used in control was replaced with lignin. The isocyanate amount was kept constant in all formulations, including the control. The isocyanate index (NCO index) for the control formulation was 80. Thirteen different formulations were prepared by only changing the lignin type. As the lignin's equivalent weight was lower than polyol, the isocyanate index for all lignin-based polyurethane foam was less than 80.

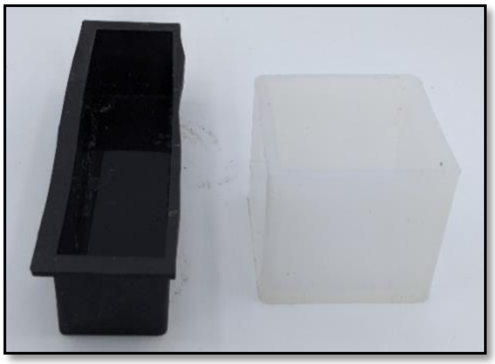


Figure 8: Silicone molds

2.2.3 Characterization of Lignin-Based Flexible PU Foam

2.2.3.1 Isocyanate Index

The amount of isocyanate required to react with the polyol and any other reactive additive (chemical blowing reagent, gelling catalyst, blowing catalyst) used in PU foam chemistry in terms of stoichiometric equivalents is called theoretical amount. This theoretically stoichiometric amount of isocyanate can then be added depending on the required foam system and final properties. The ratio of the actual amount of isocyanate used to the theoretical equivalent amount of isocyanate is known as the Isocyanate Index (Equation 2).

$$\text{Isocyanate Index} = \frac{\text{Actual amount of isocyanate used}}{\text{Theoretical amount of isocyanate required}} * 100 \qquad \text{Equation 2}$$

2.2.3.2 Apparent Density

The apparent density of the foam was determined by calculating the mass and volume of the cored foam specimen following ASTM D3574 – 17 standards. The density values obtained are specific to the part of the foam from where the specimen has been cut and (Equation 3) was used to calculate density. Dimensions of the specimen were (Length x Width x Height – 50 mm x 50 mm x 25 mm), as shown in (Figure 9). The average of at least three replicates was noted. The reported unit was in kilograms per cubic meter (kg/m$_3$) [91].

$$\text{Density} = \frac{\text{M}}{\text{V}} * 10^{6} \qquad \text{Equation 3}$$

Where:

M = mass of the specimen, g and

V = volume of the specimen, mm$_3$

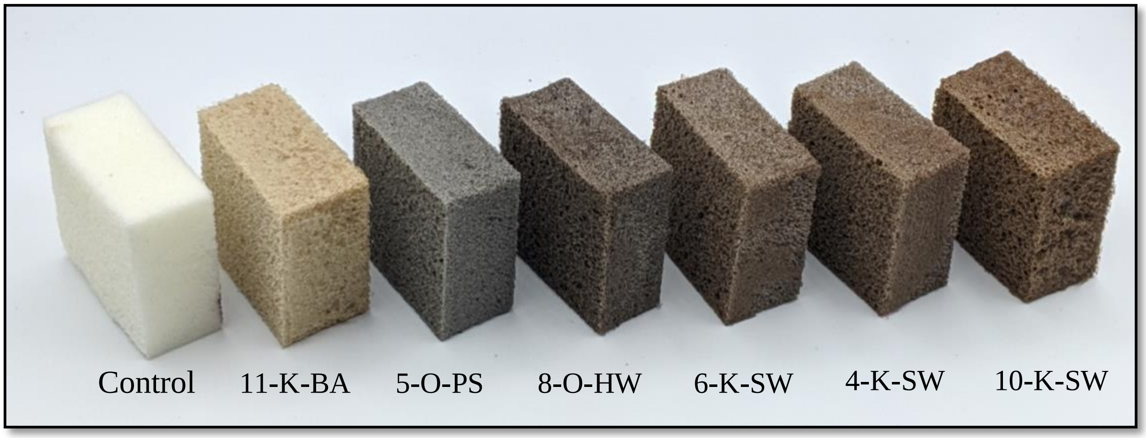


Figure 9: 20 wt% Lignin-based flexible PU foam and control foam

2.2.3.3 Tensile Strength and Ultimate Elongation

The tensile test determines the effect of a tensile force applied on the foam specimen. The specimens with dimensions of 130 mm x 30 mm (L x B) and height of 4 – 8 mm in thickness were cut from the rectangular foam slab having dimensions of 130 mm x 30 mm x 30 mm (Length x Width x Height - Figure 10). It was ensured that the foam rise was in the thickness direction, and the top and bottom surface of the specimen were parallel and free of foam skin. The edges were perpendicular to the top and bottom surface and were free of frayed areas. An Instron 5565 Universal Testing Machine was used to determine the tensile strength (kpa) and the ultimate elongation (%) (Figure 11). The test was performed based on the ASTM D3574 – 17 standards with slight modification in the specimen shape. The procedure specified a minimum grip separation of 62.5 mm. The specimen was placed in the grip of the testing machine and cautiously adjusted to a symmetrical, vertical position to ensure that the tension would be distributed uniformly over the entire cross-section. The test was performed at a grip crosshead separation speed of 500 ± 50 mm/min. When the specimen ruptured, elongation was recorded to the nearest 10% of the grip separation distance.

Tensile strength was calculated by dividing the maximum breaking force by the original cross-sectional area of the foam specimen. Ultimate elongation was measured using (Equation 4) [91]. At least three replicates per formulation were tested, and the average values were reported.

$$\%\ \text{Ultimate Elongation} = [\frac{d_f - d_o}{d_o}] \qquad \text{Equation 4}$$

Where:

d_o = original distance between grips (Which was set to 62.5 mm in all the tests)

d_f = distance between the grips at rupture/breakpoint

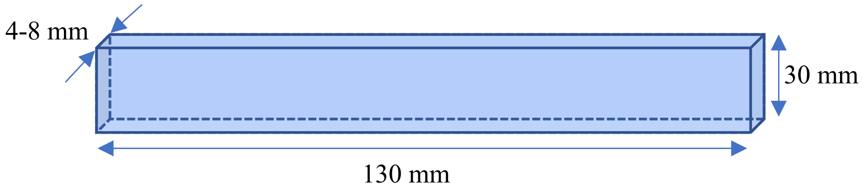


Figure 10: Dimensions of Foam used for Tensile Strength

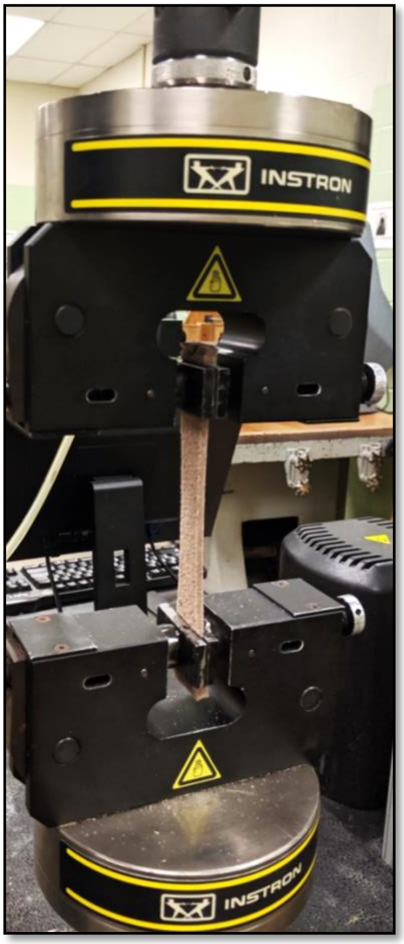


Figure 11: Tensile strength test using Instron 5565 Universal Testing Machine

2.2.3.4 Tear Strength

Tear test determines the resistance to tear propagation in the foam. This test is also performed on the Instron Universal 5565 testing Machine, which will specify the maximum force at which the specimen's rupture occurs. The test specimens were cut according to the block shape free of any skin, voids, and densification lines. The bandsaw was used to cut from a slab, ensuring that sides are parallel and perpendicular to each other. A cut of 40 mm was placed on one side, as shown in (Figure 12). The cut was made using a sharp blade so that the tear propagates evenly through the center of the block. The length of the specimen was 130 mm, and the thickness can be adjusted based on the sample quantity. Thickness was determined for each sample using the Vernier caliper to the nearest 0.01 mm precision.

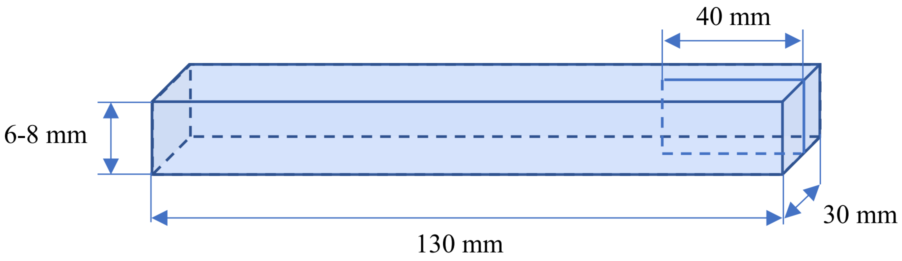


Figure 12: Tear resistance test sample (Block Shape)

The test is done following the ASTM D3574 standards with slight modification in the test specimen shape. The specimen is clamped in the jaws of the Instron 5565 Universal testing machine, ensuring that the jaws grip the specimen uniformly and adequately (Figure 13). Each tab of the block is spread to be held in the jaw to pull across the specimen. The crosshead speed of grip separation was 500 ± 50 mm/min (Figure 14). After the tear propagates through the specimen for at least a 50-mm length in the center of the block, the maximum force in Newton was recorded from the force vs. extension curve. Tear strength was calculated using maximum force registered on the Instron 5565 Universal testing Machine and the average thickness of the specimen as given by Equation 5.

$$\text{Tear strength}\left(\frac{\text{N}}{\text{m}}\right) = \frac{\text{F}}{\text{T}} * 10^3 \qquad \text{Equation 5}$$

Where:

F = force, N, and

T = thickness, mm

At least three replicates per formulation were tested, and the average values were reported in newtons per meter.

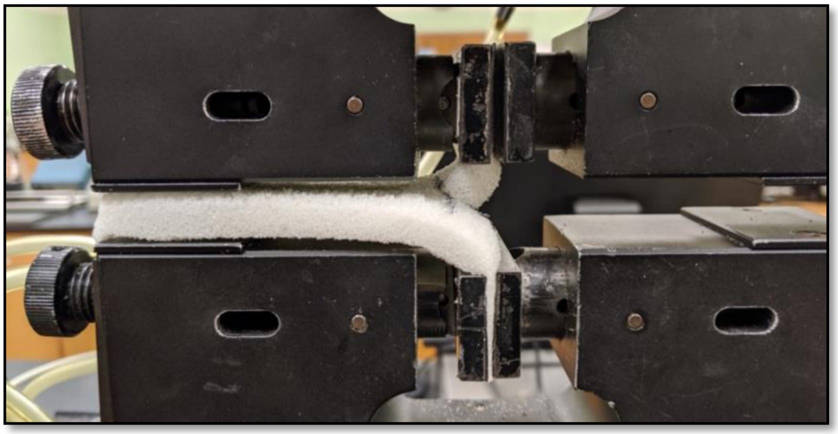


Figure 13: Specimen clamped for the tear test

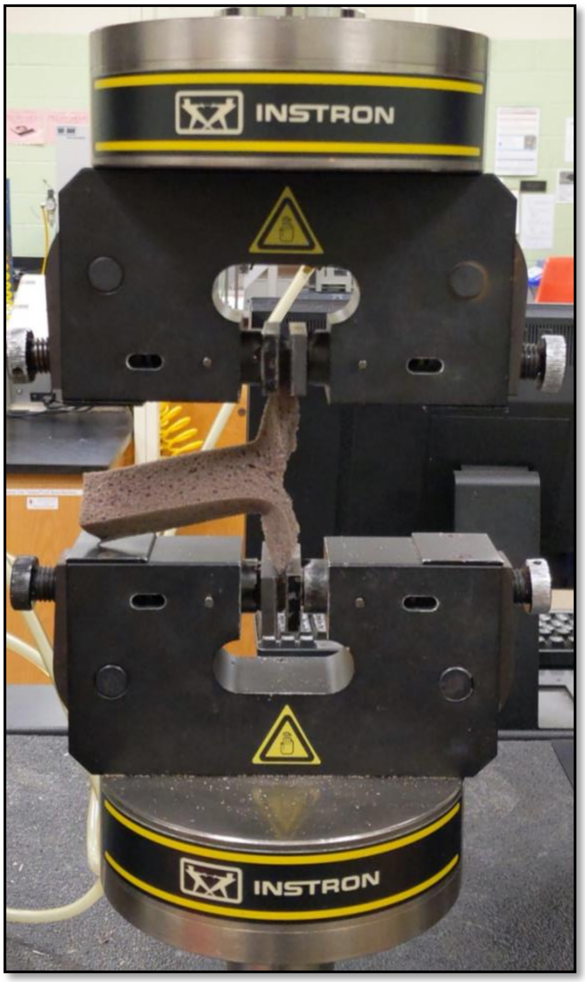


Figure 14: Tear test using Instron 5565 Universal Testing Machine

2.2.3.5 Compressive Force Deflection (CFD, at 50 % compression)

Compressive force-deflection (CFD) measures the force needed to produce a 50% compression over the entire upper area of the foam specimen. For this test, the Instron 5565 Universal testing machine was used (Figure 15). The test specimen had the standard dimension of 50 mm x 50 mm x 25 mm (height) prescribed in the ASTM D 3574 -17 test method. The test was performed by centrally placing the specimen aligned in the axial load line on the compression foot. A preflex compression was applied to the sample twice, to a deflection of 75% to 80% of the original thickness by lowering and raising the compression foot at a rate of 250 ± 25 mm/min.

During each preflex, the compression foot was allowed to clear off the specimen fully. After the final preflex, the specimen was allowed to rest for a period of 6 ± 1 min. The last step was to bring the foot into contact with the specimen at a rate of 50 ± 5 mm/min until the contact load to the specimen area became 140 ± 14 Pa. Finally, the specimen was compressed at a rate of 50 ± 5 mm/min to 50% of its original thickness, and the final force was recorded, in N, after 60 ± 3 s, while keeping the specimen compressed. Compression force-deflection, reported in kpa, was calculated using the following (Equation 6).

$$\text{Compression Force Deflection, kpa} = \frac{[\text{force, in N} * 10^3]}{\text{specimen area, in mm}^2} \qquad \text{Equation 6}$$

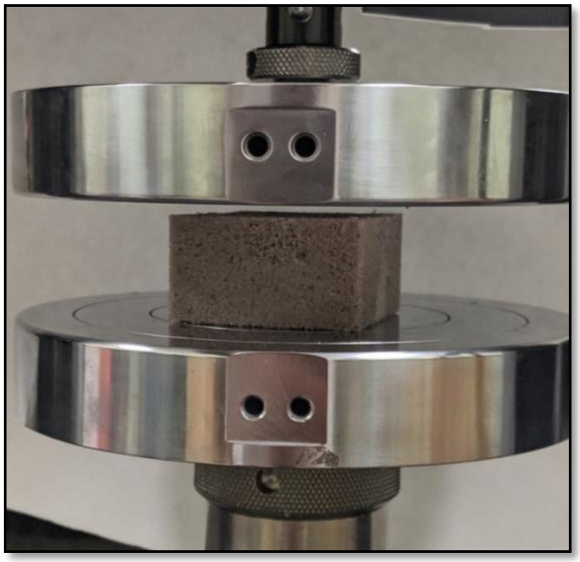


Figure 15: Compression Force Deflection Specimen set-up

2.2.3.6 Compression Modulus

The compression modulus was calculated from the compression stress versus strain (extension) curve along the parallel direction of foam growth using Instron 5565 Universal testing machine at 50.0 mm/min compression rate and was analyzed with Bluehill® software. The compression stress at a 5-6 % compression strain was used to calculate the compression modulus of samples. The dimension of the sample used was 50 × 50 × 25 mm_3, and the mean of at least three replicates were reported in kpa.

2.2.3.7 Support (Sag) Factor

The support factor (the ratio of 65 % CFD and 25 % CFD values) was calculated to evaluate the cushioning performances of foams. For this test, an Instron 5565 Universal testing machine having a flat, fixed compression foot bigger than the size of the specimen was connected to a force determining device. The test specimen had standard dimensions of 50 mm x 50 mm x 25 mm (height) prescribed in the ASTM D 3574 -17 test method. The test was performed by centrally placing the specimen aligned in the line of axial load on the compression foot. A preflex was applied on the specimen twice, to a deflection of 75% to 80% of the original thickness by lowering and raising the compression foot at a rate of 250 ± 25 mm/min. During each preflex, the compression foot was allowed to clear off the specimen fully. After the final preflex, the specimen was permitted to rest for a period of 6 ± 1 min. The last step was to bring the foot into contact with the specimen at a rate of 50 ± 5 mm/min till the contact load to the specimen area becomes 140 ± 14 Pa. Finally, the specimen was compressed at a rate of 50 ± 5 mm/min to 25% of its original thickness, and the final force was recorded, in N, after the 60 ± 3 s while keeping the specimen compressed. Similarly, 65% compression force was recorded, and the support factor was calculated using the following (Equation 7).

$$\text{Support factor} = \frac{\text{CFD } 65\%}{\text{CFD } 25\%} \qquad \text{Equation 7}$$

2.2.3.8 Compression Set

This test method comprises compressing the foam sample to a specified deflection, with specific temperature and duration, and then evaluating the change in the height of the specimen after a certain recovery period. The compression device comprises two flat, stiff metal plates arranged in such a manner that the plates are parallelly facing each other using clamps. The space between the plates is modifiable to the required compression using spacers.

All measurements, conditioning, and recovery of the test specimens were conducted at room temperature (23±2°C) and following ASTM D3574 – 17 standards. The test specimen was cut using a band saw to get the dimensions of 50 mm x 50 mm x 25 mm (height), and it had parallel top and bottom surfaces. The test specimens were placed in the compression device, and the plates were deflected to 6mm thickness, which was approximately 75 ± 1 % of their original thickness using a spacer and the clamps. It was ensured that the specimens were placed in such a way that there was at least 6 mm separation in all directions when compressed between two plates. The compression set up containing a deflected specimen was placed in the oven at 60 ± 2°C for 22 hours. After that, the compression device was taken out of the oven, and the samples were removed immediately, allowing them to recover for 30 to 40 min. The final thickness of the test specimen was measured precisely using the Vernier calipers, and the following (Equation 8) was used to calculate the compression set values.

$$C_d = \left[\frac{t_o - t_f}{t_o - t_s}\right] * 100 \qquad \text{Equation 8}$$

where:

C_d: compression set expressed as a percent of the original deflection,

t_o: the original thickness of the test specimen,

t_s: the thickness of spacer bar used, and

t_f: the final thickness of the test specimen.

At least three replicates per sample were tested, and their average and the standard deviation were reported.

2.2.3.9 Thermal Behavior (TGA)

A Thermogravimetric Analyzer (TGA Q50) from TA instruments was used to measure the thermal degradation properties of the lignin-containing PU flexible foams. The samples were taken from the core of the foam. The specimens were heated from room temperature to 600 °C at a rate of 20 °C/min in a nitrogen atmosphere. The temperature of onset, the temperature of offset, and temperature at maximum weight loss were reported.

2.2.3.10 Cell Size Distribution Analysis

A Dino-Lite Edge Digital Microscope was used to measure the cell size of each foam sample. Cell size was calculated by averaging the size of at least ten cells from formulated foams perpendicular to the foam rise. The polarization of the microscope was adjusted for each sample based on color to obtain better pictures for cell size analysis.

2.2.3.11 Statistical Analysis

The results were analyzed using SAS university edition software to check the analysis of variance (ANOVA), and Tukey's honestly significant difference (Tukey's HSD) test with a 95% confidence level to calculate the significant differences between means. The correlations between lignin properties and lignin-based flexible foam performance were also analyzed using the Pearson correlation matrix.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 RESULTS AND DISCUSSION

Lignin based flexible PU foam with 20 wt% lignin loading and a control formulation without lignin were characterized by measuring their physical, mechanical, and thermal properties. Physical properties included density and cell morphology. Mechanical properties comprise of tests to assess the effect of mechanical stress on the flexible PU foam, such as tensile strength, compression force deflection, and tear strength tests. Thermal properties were measured using TGA to analyze the stability of the lignin-based PU foam at higher temperatures.

3.1.1 Isocyanate index (NCO index) of flexible PU foam

The control flexible PU foam had an isocyanate index of 80. Lignin-based foams were made using the procedure given in the experimental section (2.2.2). In lignin-based foam formulations, conditions remained identical to the control (foam without lignin), except that 20 wt% of polyol was replaced with different lignins. Therefore, the isocyanate index for each lignin-based foam changed according to the OH value of the respective lignin. Hydroxyl (OH) values of lignins were higher than the polyol used in the control foam formulation while using the same amount of isocyanate; lignin-based flexible PU foams had NCO indexes less than 80 as shown in (Table 6). Hydroxyl (OH) values of the lignins were calculated using the $_{31}$P-NMR and data is given in (APPENDIX A)

Table 6: OH values and isocyanate indexes of flexible PU foam foamulations

Lignin #	Process	Source	OH Value* (mg KOH/g)	NCO Index
-	Control	Control	28	80.0
1	Kraft	Softwood	315	61.3
2	Organosolv	Hardwood	256	64.4
3	Organosolv	Corn Stover	219	66.5
4	Kraft	Softwood	332	60.4
5	Organosolv	Peanut Shell	191	68.2
6	Kraft	Softwood	321	61.0
7	Kraft	Softwood	301	62.0
8	Organosolv	Hardwood	229	65.9
9	Lignosulfonate	Softwood	65	77.0
10	Kraft	Softwood	376	58.4
11	Kraft	Bagasse	272	63.5
12	Kraft	Softwood	360	59.1
13	Kraft	Softwood	293	62.4

3.1.2 Apparent Density

Apparent density is an essential parameter in the final PU flexible foam, as lightweight material will consume less energy and improve the overall efficiency in automotive applications. Therefore, lower density foam with better mechanical properties is preferred. This test was done according to ASTM D 3574 standards. The average of at least three replicates was reported (Figure 16). After partially substituting the polyol with unmodified lignin, the apparent density of lignin-containing PU flexible foams significantly increased compared to the control foam prepared without lignin. The density of the control foam was around 60 kg/m$_3$, while lignin-based foams prepared by replacing 20% of the polyol with different lignins had the density range between 63-100 kg/m$_3$ (Figure 16). The standard acceptable density for the automotive applications, especially for the panel insulator or floor carpet, is between 30-90 kg/m$_3$. All the lignin-based foams except 9-L-SW and 10-K-SW had a density lower than 90 kg/m$_3$. Tukey's grouping helped to group different lignins with the apparent densities that were not significantly different from each other. For instance, there was no significant difference between the density of the foams prepared with lignins 5-O-PS, 8-O-HW, 3-O-CS, 13-K-SW, 6-K-SW, 11-K-BA and the apparent density of control foam (without lignin), as shown in (Figure 17).

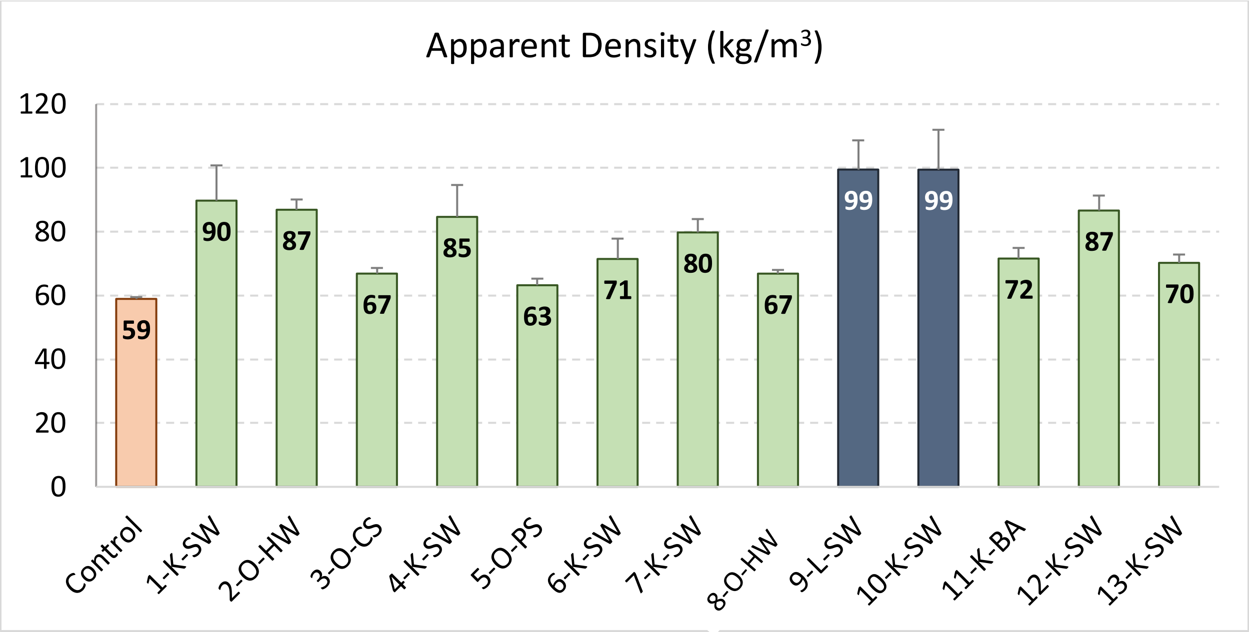
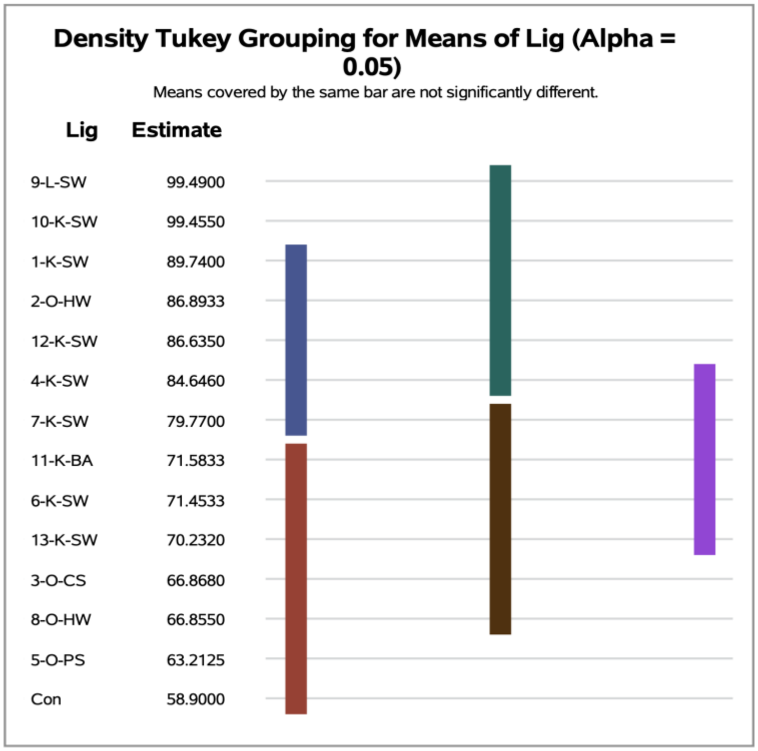


Figure 16: Apparent density of 20% lignin-based foams and control (without lignin)



Density Tukey Grouping for Means of Lig (Alpha = 0.05)

Means covered by the same bar are not significantly different.

Lig	Estimate
9-L-SW	99.4900
10-K-SW	99.4550
1-K-SW	89.7400
2-O-HW	86.8933
12-K-SW	86.6350
4-K-SW	84.6460
7-K-SW	79.7700
11-K-BA	71.5833
6-K-SW	71.4533
13-K-SW	70.2320
3-O-CS	66.8680
8-O-HW	66.8550
5-O-PS	63.2125
Con	58.9000

Figure 17: Tukey grouping of the density analysis of lignin-based flexible foam

3.1.3 Tensile Strength and Ultimate Elongation

Tensile strength tests were performed to determine the effect of tensile stress on the lignin-based PU foam. The test was performed according to ASTM D 3574 standards with a slight modification to test specimen dimensions. The tensile strengths of all the lignin-based foams were either in the same range as of control or higher than control, as shown in (Figure 18). The control formulation had a tensile strength of 64 kPa, and the lignin-based foams had the tensile strength in the range of 50-120 kPa. The standard range of tensile strengths for the automotive applications, especially for the panel insulator or floor carpet, is in the range of 50 – 200 kPa. All the lignin-based foams with a 20% replacement surpassed the standard minimum value (50 kPa), as seen in (Figure 18). The increase in tensile strength is due to the aromatic structure of lignin and their higher hydroxyl value compared to the polyol (used in this study, 28 mgKOH/g), which results in a higher degree of crosslinking [92], as also observed by previous studies [93].

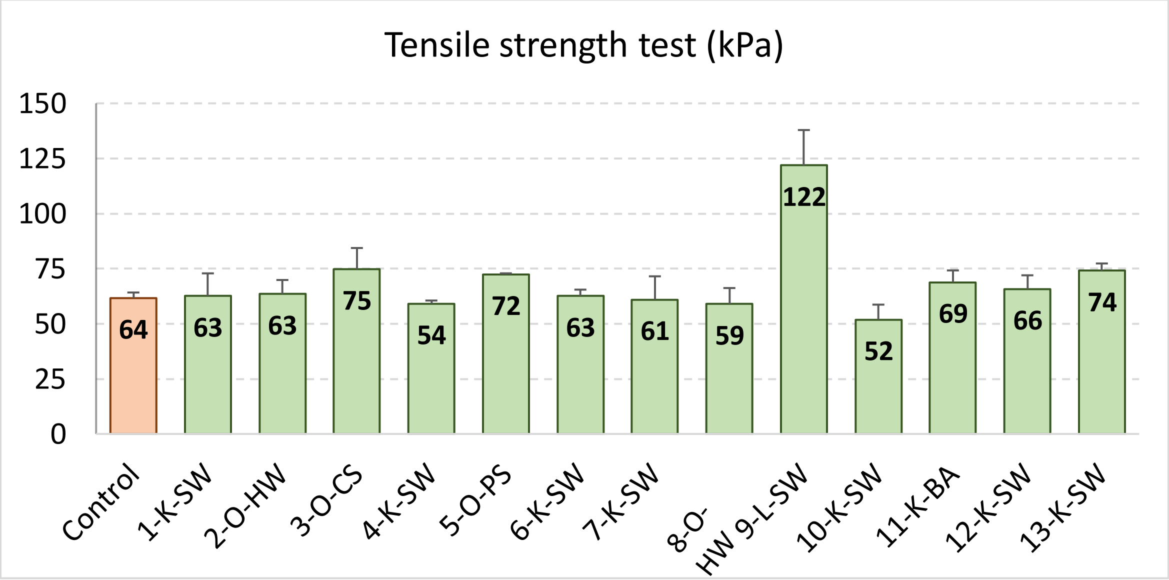


Figure 18: Tensile strength (kPa) of 20% lignin-based foams and control (without lignin)

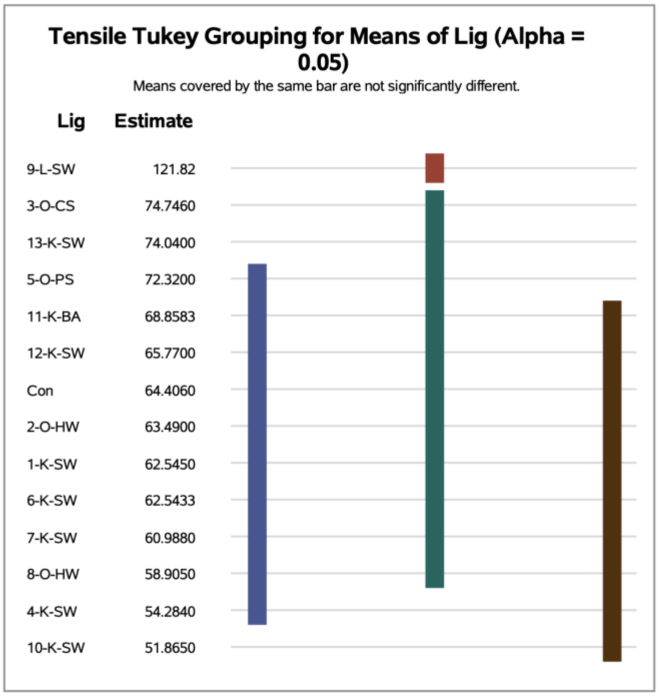


Figure 19: Tukey Grouping for the Tensile Test of Lignin-Based Flexible Foam

As shown in (Figure 20), the control formulation had an ultimate elongation of 124%, while the elongation of lignin-based flexible PU foams was in the range of 40-80%. The ultimate elongation of PU flexible foams reduced significantly after the addition of lignin. This decrease in the ultimate elongation values are potentially due to the fact that the polyol used in the control formulation has a long aliphatic chain, which gives the foam its flexibility and elasticity. In contrast lignin has aromatic structures [4]. Replacing the soft segment (polyol portion) of the foam with lignin, which has high T_g values (95-150 °C), increase the brittleness of the polyurethane flexible foam [73]. It was also reported in the literature that higher functionality increases crosslinking and decreases the ultimate elongation, which corroborates with the data for lignin-based flexible PU foams [4]. The standard range for the ultimate elongation for the automotive application (panel insulator or floor carpet) is 60 – 105 %. Among tested lignins, all the lignin-based foams except four of them (4-K-SW, 9-K-SW, 10-K-SW, and 12-K-SW) meet the standard requirement acceptable for automotive application.

Tukey grouping (Figure 21) clearly showed that the lignin incorporation had a significant effect on the foam formulation, and the values of ultimate elongation for the lignin-based foams were significantly different from the control PU foam.

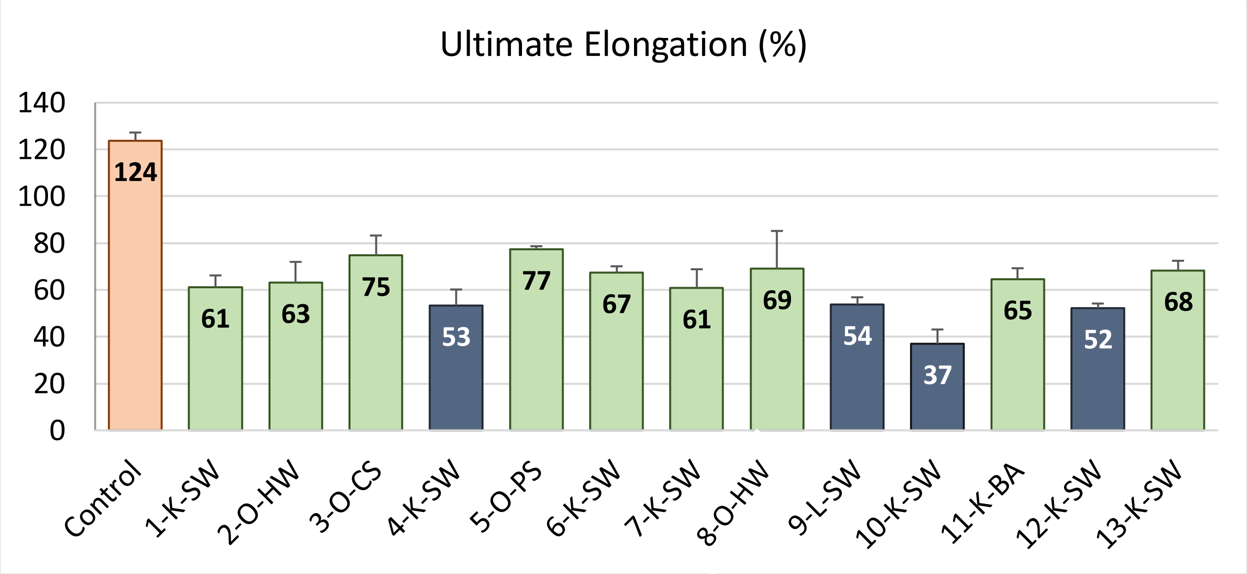


Figure 20: Ultimate elongation of 20% lignin-based foams and control (without lignin)

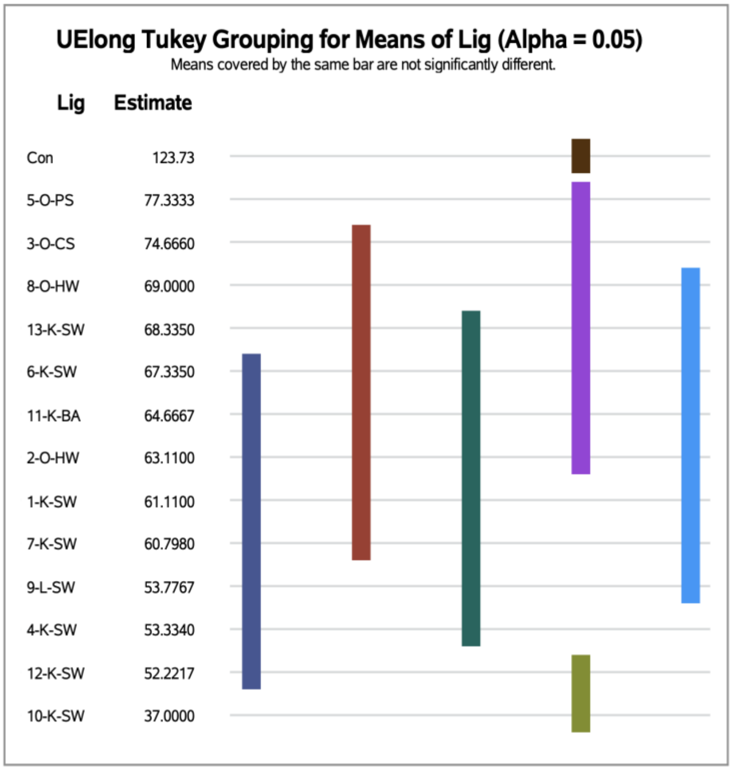


Figure 21: Tukey Grouping for the Ultimate elongation of lignin-based flexible foam

3.1.4 Tear Strength

The primary purpose of performing the tear strength test on flexible polyurethane foam is to determine the peak force when a tear propagates through the foam. This test measures the material's resistance to tear propagation. Overall, lignin-based flexible PU foams performed better compared to the control formulation, as shown by (Figure 22). The standard requirement for the automotive application, especially for the panel insulator and floor carpet, is in the range of 200-1000 N/m. All the lignin-based foams surpassed the minimum requirement of 200 N/m., Based on the Tukey's grouping it was evident that there was no significant difference between the lignin-based foams' tear strengths, except for lignin 9-L-SW with the control foam (Figure 23).

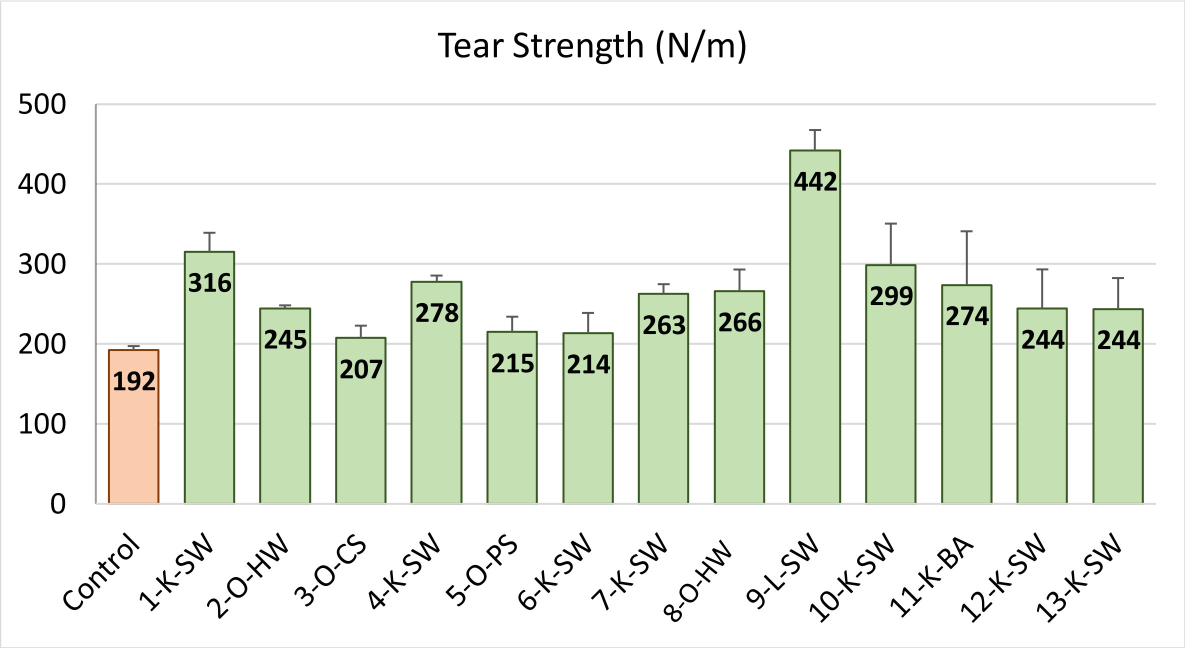
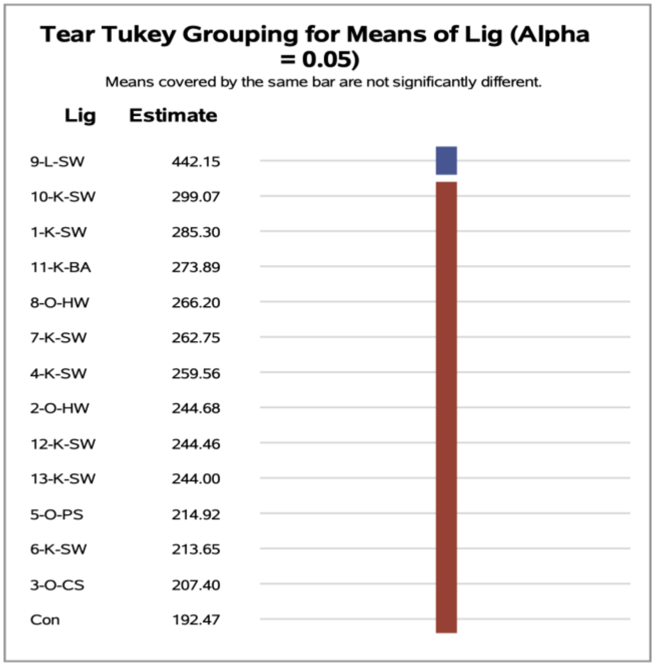


Figure 22: Tear strength (ASTM D 3574) of 20% lignin-based foams and control (without lignin)



Tear Tukey Grouping for Means of Lig (Alpha = 0.05)

Means covered by the same bar are not significantly different.

Lig	Estimate
9-L-SW	442.15
10-K-SW	299.07
1-K-SW	285.30
11-K-BA	273.89
8-O-HW	266.20
7-K-SW	262.75
4-K-SW	259.56
2-O-HW	244.68
12-K-SW	244.46
13-K-SW	244.00
5-O-PS	214.92
6-K-SW	213.65
3-O-CS	207.40
Con	192.47

Figure 23: Tukey Grouping for the Tear Strength of Lignin-Based Flexible Foam

3.1.5 Compression Force Deflection (CFD)

ASTM D3574 standard was used to measure the force of compression required to produce a deflection of 50% (with respect to original height) over the entire top surface of the test specimen. This analysis provides a better method for comparing and characterizing different foam specimens to determine their ideal applications. Compression force deflection (CFD) values of PU foams for 50% compression with different lignin replacement are summarized in (Figure 24). Compression moduli for foams were determined using compressive force-deflection stress-strain curves with a crosshead speed of 50 mm/min. The initial Hookean region of the curves was used for each sample and was manually analyzed for the range of 5 - 6 % strain. The compression moduli (Figure 26) and the CFD values (Figure 24) of the PU foams were either similar to control or increased when 20% of polyol was replaced with lignin. This behavior was in agreement with the previous studies done on determining the effect of lignin on the mechanical properties of flexible foam [60]–[62]. The main reason for the change in mechanical properties, especially CFD, is that lignin-based foams had lower isocyanate indexes (Table 6), resulting in foams with potentially higher amounts of urethane linkages, thus strengthening the struts of lignin-containing PU flexible foams [50].

Moreover, lignin consists of a higher amount of phenolic (aromatic) structures, which form a hard segment reinforcing the PU flexible foams. It was reported in the literature that lignin could act as a filler as well as the crosslinking reagents in the PU flexible foam [50], [58]. Therefore, the mechanical properties (CFD, compression modulus) are also increased by the filler-matrix interaction within the lignin-based PU flexible foams [94]. The acceptable range for the compression force deflection test was in the range of 3 -12 kPa for the floor carpet and insulator application in the automotive industry. CFD values of all but four lignin-based foams (1-K-SW, 9-L-SW, 10-K-SW, and 12-K-SW, indicated with grey bars, in (Figure 24) were in the acceptable range. Based on the Tukey grouping for the CFD (Figure 25) and compression modulus (Figure

27), it was evident that lignin had a significant effect on the foam mechanical properties (P-value < 0.0001).

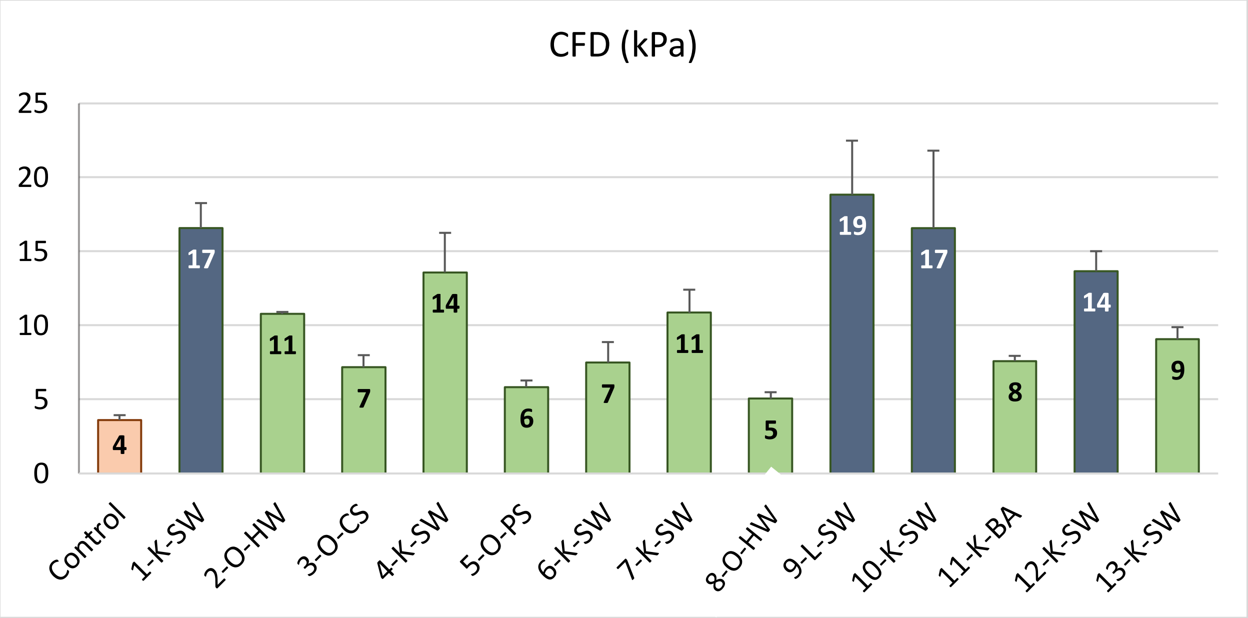
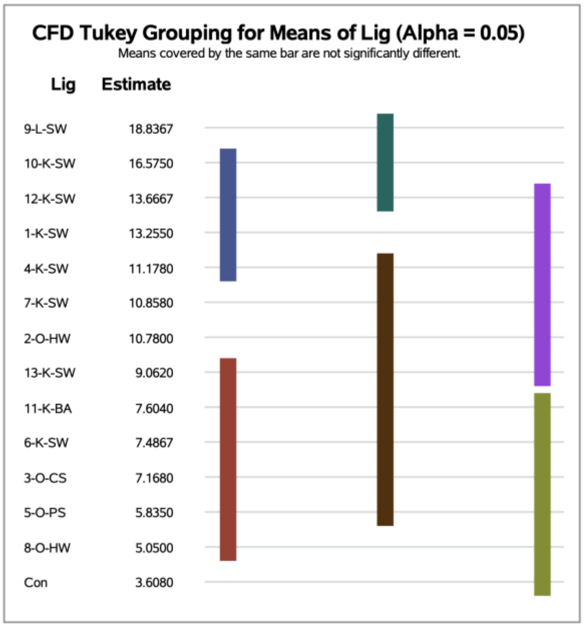


Figure 24: Compression Force Deflection test (ASTM D 3574) of 20% lignin-based foams and control (without lignin)



CFD Tukey Grouping for Means of Lig (Alpha = 0.05)

Means covered by the same bar are not significantly different.

Lig	Estimate
9-L-SW	18.8367
10-K-SW	16.5750
12-K-SW	13.6667
1-K-SW	13.2550
4-K-SW	11.1780
7-K-SW	10.8580
2-O-HW	10.7800
13-K-SW	9.0620
11-K-BA	7.6040
6-K-SW	7.4867
3-O-CS	7.1680
5-O-PS	5.8350
8-O-HW	5.0500
Con	3.6080

Figure 25: Tukey Grouping for the CFD values of lignin-based flexible foam

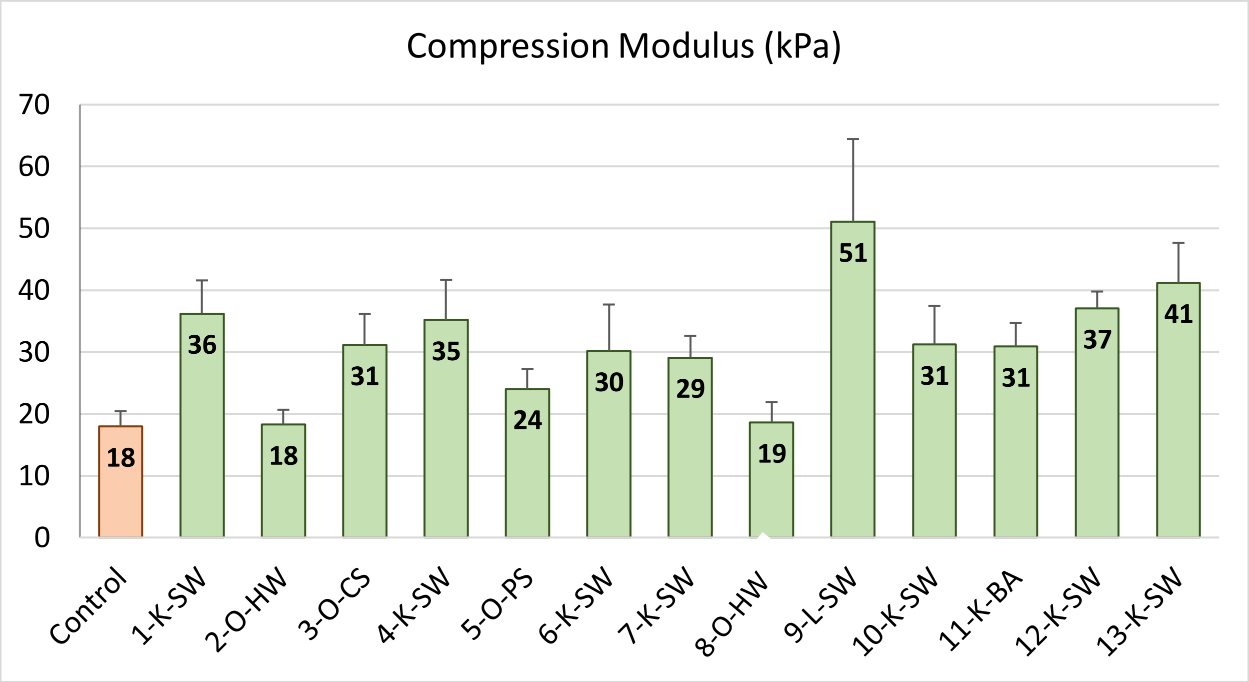
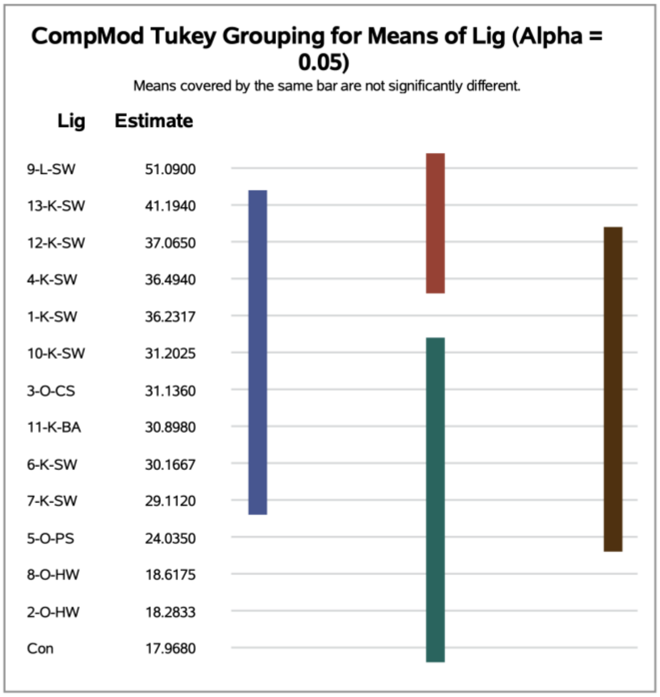


Figure 26: Compression Modulus of 20% lignin-based foams and control (without lignin)



Lig	Estimate
9-L-SW	51.0900
13-K-SW	41.1940
12-K-SW	37.0650
4-K-SW	36.4940
1-K-SW	36.2317
10-K-SW	31.2025
3-O-CS	31.1360
11-K-BA	30.8980
6-K-SW	30.1667
7-K-SW	29.1120
5-O-PS	24.0350
8-O-HW	18.6175
2-O-HW	18.2833
Con	17.9680

Figure 27: Tukey Grouping for the Compression Moduli of Lignin-Based Flexible Foam

3.1.6 Compression Set

The compression set results of flexible PU foams is presented in (Figure 28). The compression set determines the recovery ability of the flexible PU foams after being compressed under constant stress and allowing them to recover for a specified duration (after compressing for 22 hours) with specific conditions (75% compression, at 60°C). Lower the compression set value better is the foam's ability to recover. It was found that after partially substituting the polyol with unmodified lignin, the compression set of lignin-containing PU flexible foams significantly increased compared to the control formulation. The compression set result for the control foam was around 6%, while the lignin-based foams had compression set percentages between 7% - 32%, as shown in (Figure 28). The increase in the compression set is potentially due to an increase in the formation of urethane linkages as also reported in previous literature [95]. Therefore, when the specimens were kept at an elevated temperature for compression, i.e., at 60 °C the hydrogen bonds between N-H from urethane (i.e., hard segment) and O-H groups from polyol/lignin were weakened, which led to the deformation of flexible PU foams [95]. This deformation was more in lignin-based foams compared to the control (Figure 28). But, the maximum limit for automotive applications, especially for the panel insulator or floor carpet, was 60%. All the lignin-based foams had compression set values lower than the maximum limit of 60%, which means their performances were in the standard range. Based on Tukey's grouping, it was evident that all lignin-based foams except (2-O-HW, 3-O-CS, 4-K-SW, 7-KSW) had values not significantly different from the control.

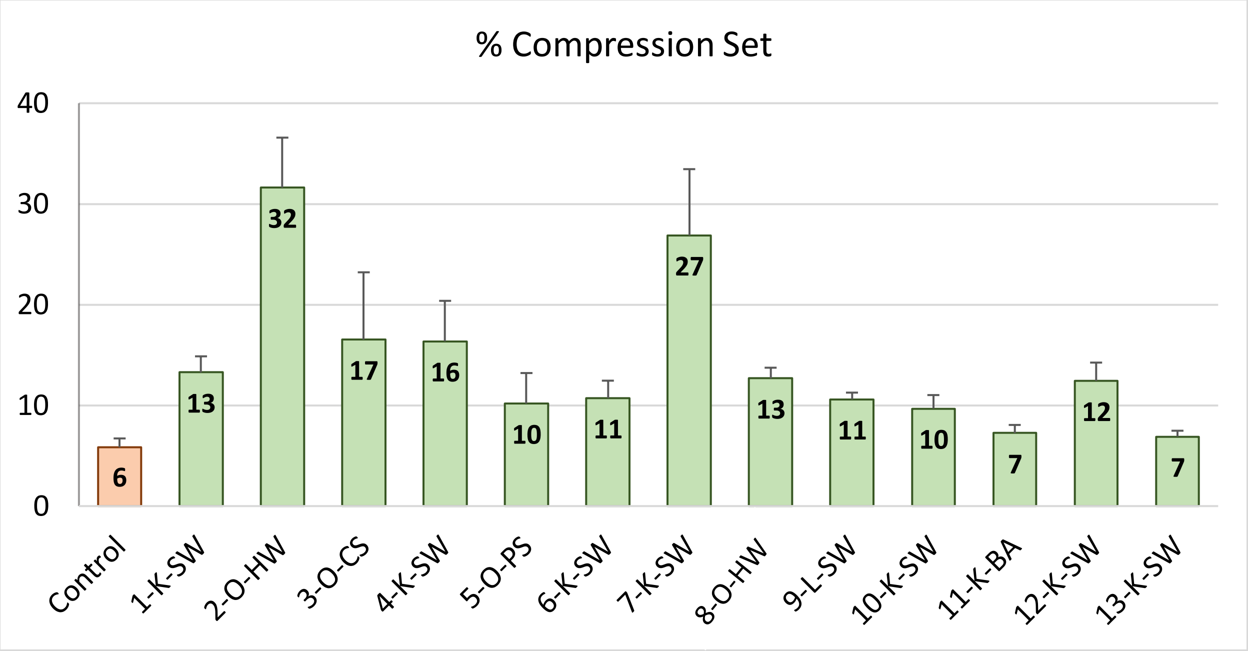
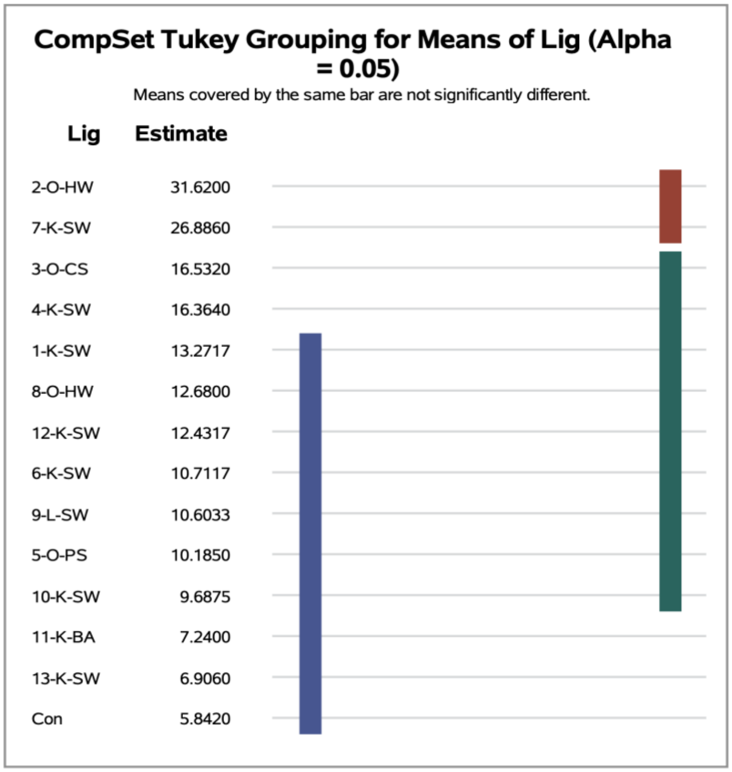


Figure 28: Compression set of 20% lignin-based foams and control (without lignin)


CompSet Tukey Grouping for Means of Lig (Alpha = 0.05)

Means covered by the same bar are not significantly different.

Lig	Estimate
2-O-HW	31.6200
7-K-SW	26.8860
3-O-CS	16.5320
4-K-SW	16.3640
1-K-SW	13.2717
8-O-HW	12.6800
12-K-SW	12.4317
6-K-SW	10.7117
9-L-SW	10.6033
5-O-PS	10.1850
10-K-SW	9.6875
11-K-BA	7.2400
13-K-SW	6.9060
Con	5.8420

Figure 29: Tukey Grouping for the Compression set of Lignin-Based Flexible Foam

3.1.7 Support (Sag) Factor

The support factor assesses the foam's ability to support the weight. It is the ratio of the 65% CFD value to 25% CFD value. Support factors for foam range from about 1.5 to 2.6 (cushioning applications). The higher the support factor, the better the ability of the foam to provide support.

Lignin-based foams had higher support (sag) factor than control foam, indicating that replacing even 20 wt% of the polyol with lignins can significantly improve the support factor of PU flexible foams (Figure 30). Tukey grouping stated that there was a significant difference in the sag factor values between the control formulation and lignin-containing foams except for lignin (13-K-SW, 3-O-CS, 9-L-SW, 11-K-BA, 5-O-PS). And all the lignin-based foams performed better compared to control.

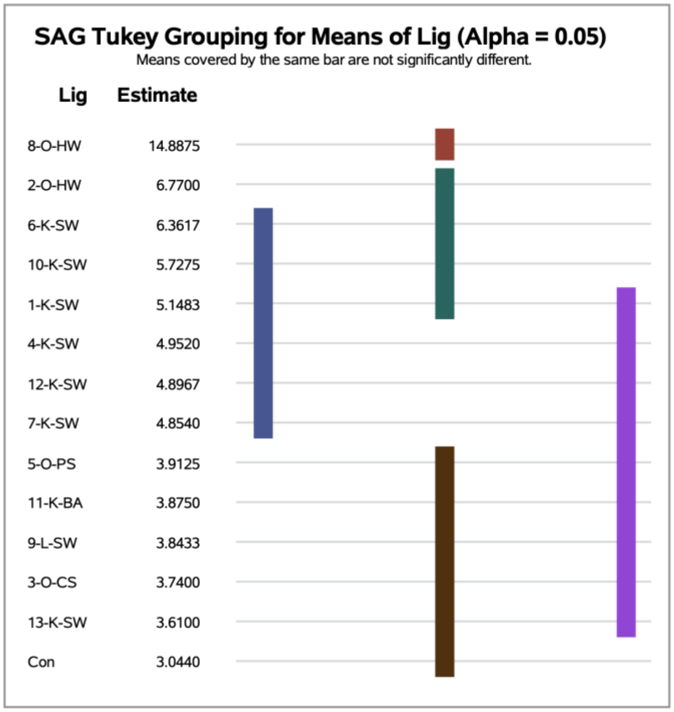


Figure 30: Tukey Grouping for Sag factor of 20% lignin-based foams and control (without lignin)

3.1.8 Thermal Behaviour

Thermogravimetric analysis (TGA) is a very useful technique for studying the degradation steps of PU materials. (Figure 31) and (Figure 32) displays the TGA curves and the derivative curves of the studied control and lignin-based PU flexible foams, respectively. The thermal degradation stages of a biobased polyurethane network have been studied through TGA [96], and it was reported that the polyurethanes show multiple (two or three) phases of degradation. The derivative curve (Figure 32) presented two degradation phases for the control foam and (1-K-SW) lignin-based foam, indicating a similar degradation mechanism. In the control formulation without lignin, the first stage of thermal degradation started around 260 °C. Conversely, in the lignin-based (1-K-SW) formulation, thermal degradation for the first stage started at a higher temperature, around 290 °C. The first degradation phase in the lignin-based foam can be associated with the irreversible cleavage of urethane bonds, which happens around 200 °C [57]. The second degradation phase at around 380 °C can be associated with the thermal degradation of soft segments, as reported in the literature [97].

To assess the thermal stability of the lignin-based foams, the temperature of onset (T_{onset}), the temperature of offset (T_{offset}), and temperature at maximum degradation (T_{max}) were recorded using Thermogravimetric analysis (TGA) Q50 instrument summarized in (Table 7) and (Figure 33). It was found that after partially substituting the polyol with unmodified lignin, T_{onset}, T_{offset}, and T_{max} of lignin-containing PU, flexible foams increased compared to the control formulation. T_{max} for the control foam was 374 °C, while lignin substituted foam had T_{max} in the range of 375-395 °C. Based on the acquired data, it was evident that lignin-based flexible PU foams had higher thermal stability than the control foam (Table 7)

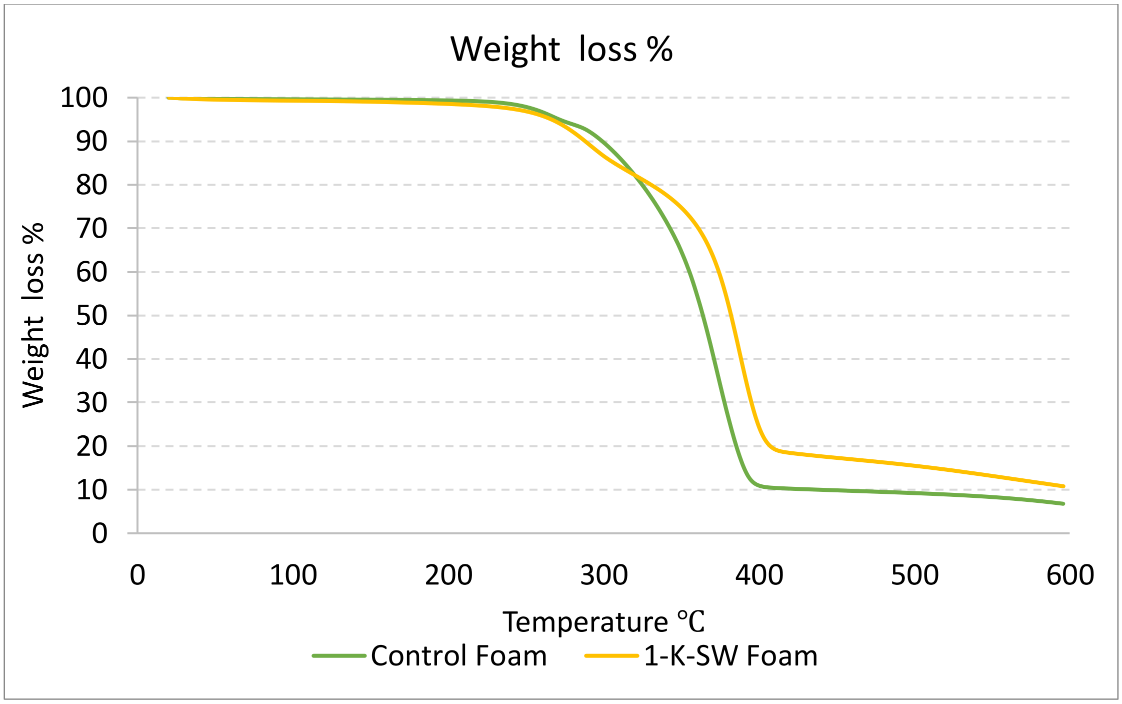


Figure 31: TGA curve of the produced PU flexible foams. All thermograms were acquired at the constant heating ramp of 10 °C/min in a nitrogen atmosphere

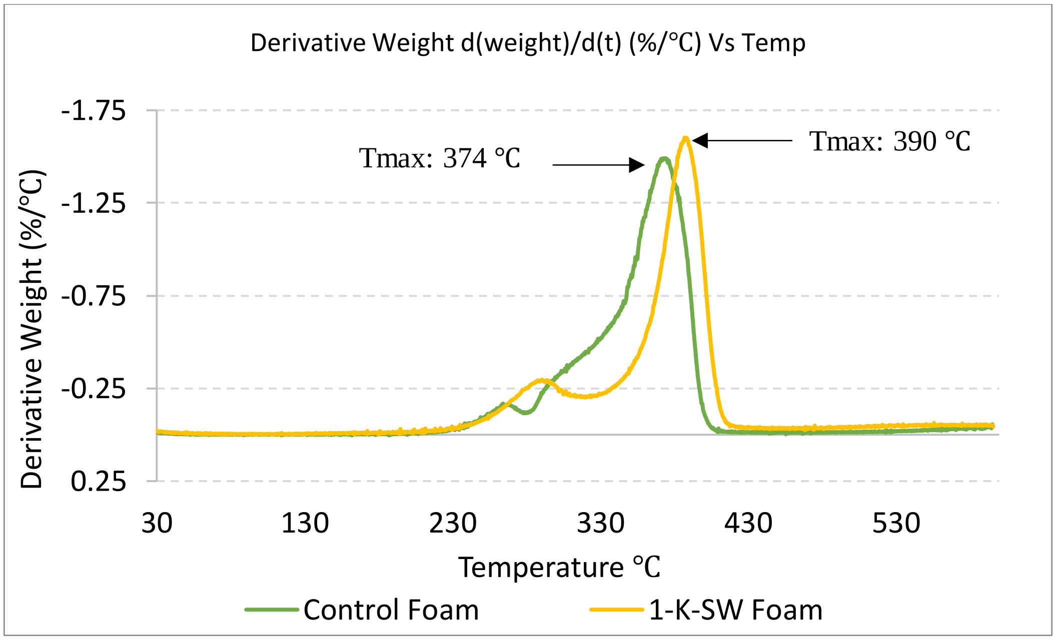


Figure 32: Derivative TGA curve of the produced PU flexible foams. All thermograms were acquired at the constant heating ramp of 10 °C/min in a nitrogen atmosphere

Table 7: T_{onset} and T_{offset} data for the TGA curves of 20% lignin-based foams and control (without lignin)

Lignin	T_{onset} (°C)	T_{offset} (°C)
Control	331.1 ± 0.01	390.4 ± 0.9
1-K-SW	355.9 ± 5.2	403.1 ± 5.0
2-O-HW	354.4 ± 0.9	406.4 ± 1.9
3-O-CS	345.2 ± 4.5	399.7 ± 4.4
4-K-SW	352.3 ± 3.5	399.0 ± 3.7
5-O-PS	344.0 ± 2.3	401.4 ± 2.8
6-K-SW	354.8 ± 1.6	406.7 ± 2.6
7-K-SW	352.9 ± 9.1	401.7 ± 8.3
8-O-HW	353.4 ± *	402.7 ± *
9-L-SW	343.9 ± 2.0	399.8 ± 5.4
10-K-SW	344.9 ± 2.3	392.3 ± 3.8
11-K-BA	331.3 ± 13.2	395.5 ± 5.6
12-K-SW	351.8 ± *	400.4 ± *
13-K-SW	363.0 ± 1.5	412.0 ± 6.2

* More replicates will me measure as soon as the lab reopens

Note: SW = Softwood, HW = Hardwood, PS = Peanut Shell, CS = Corn Stover, K= Kraft, O = Organosolv, L = Lignosulfonate, BA = Bagasse

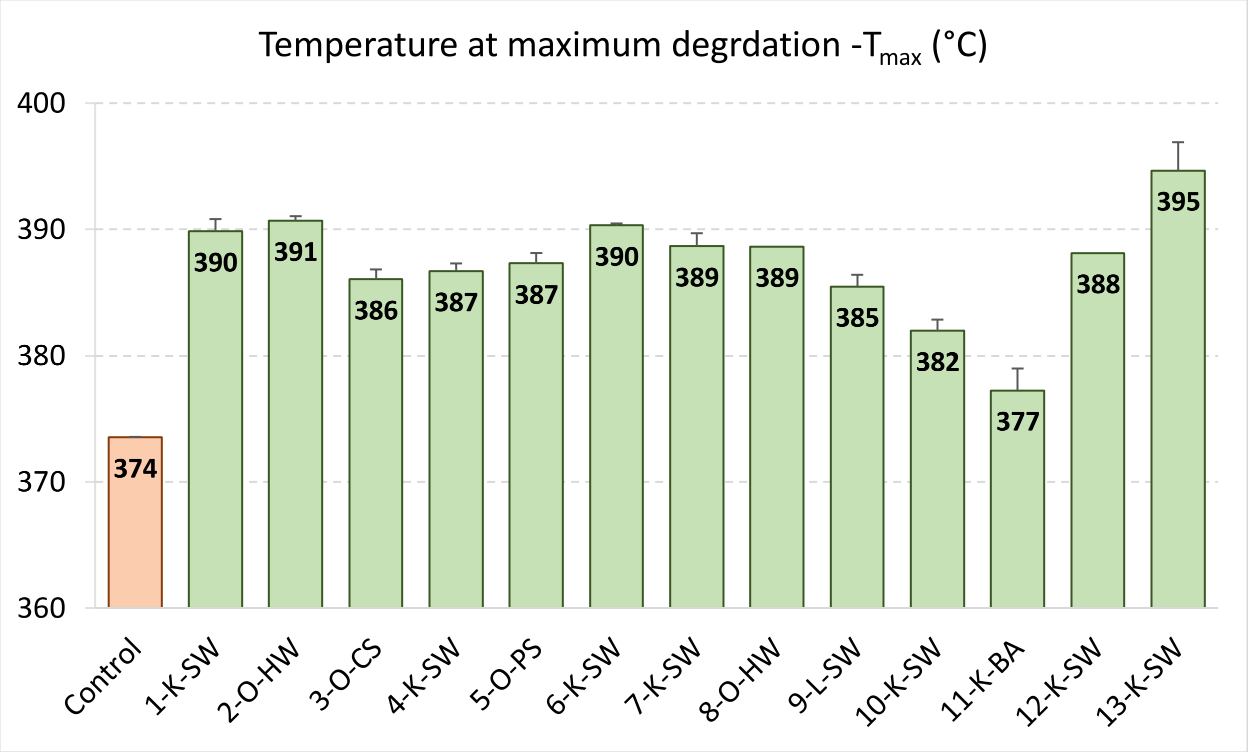


Figure 33: Temperature at maximum degradation of 20% lignin-based foams and control (without lignin)

3.1.9 Cell size

It is important to study the morphological changes in the foam after lignin addition. Quick and straightforward imaging analysis was done using the microscope to determine the average cell size of the open cells present in the flexible PU foam. Lignin-containing foams with 20 wt% polyol replacement had cell sizes in the range of 270-350 µm (Figure 34), and the control formulation had the cell sizes of 344 ± 27 µm. A Tukey test showed that there was no significant difference between the values of the average cell size of lignin-based foams and control foam (Figure 35).

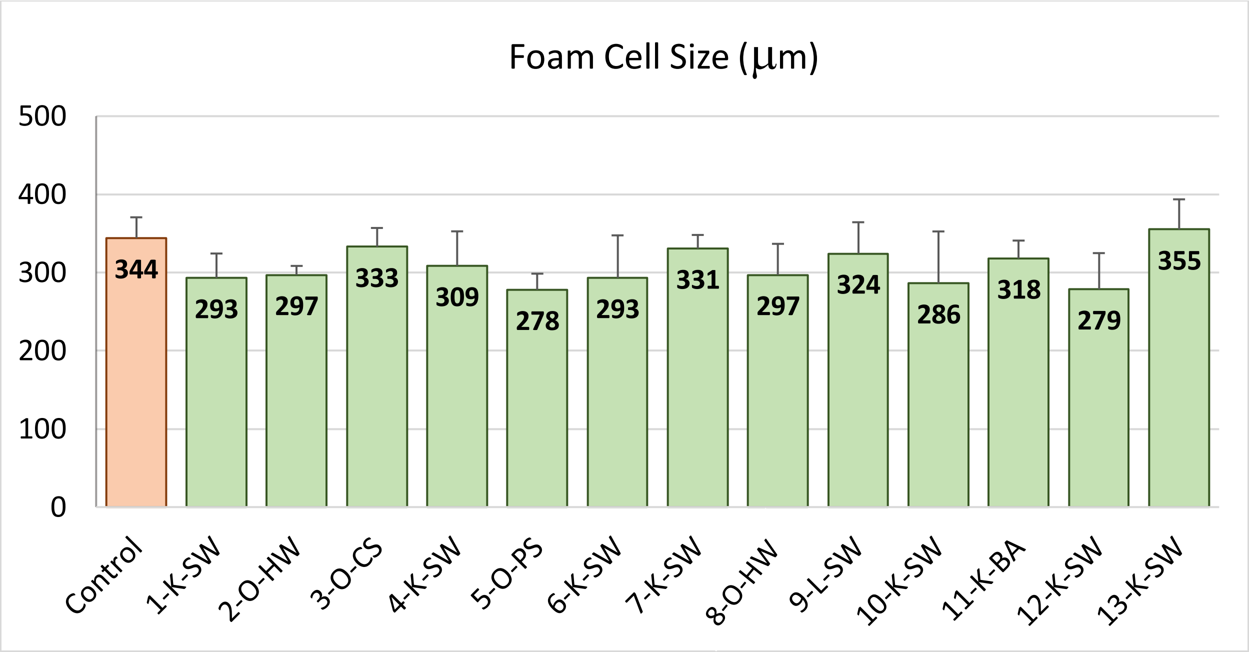
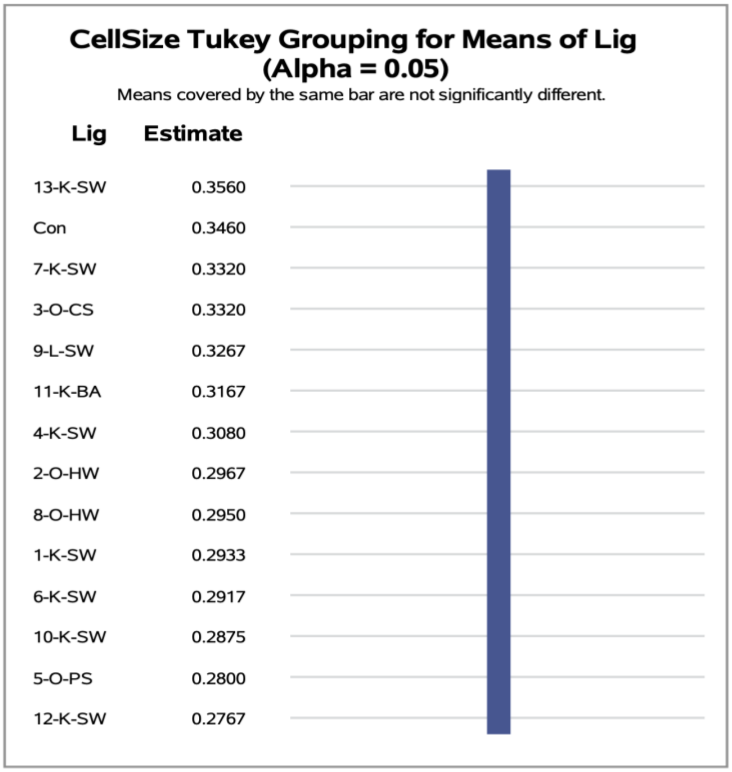


Figure 34: Cell Size of 20% lignin-based foams and control (without lignin)



CellSize Tukey Grouping for Means of Lig
(Alpha = 0.05)

Means covered by the same bar are not significantly different.

Lig	Estimate
13-K-SW	0.3560
Con	0.3460
7-K-SW	0.3320
3-O-CS	0.3320
9-L-SW	0.3267
11-K-BA	0.3167
4-K-SW	0.3080
2-O-HW	0.2967
8-O-HW	0.2950
1-K-SW	0.2933
6-K-SW	0.2917
10-K-SW	0.2875
5-O-PS	0.2800
12-K-SW	0.2767

Figure 35: Tukey Grouping for the Cell Size of Lignin-Based Flexible Foam

3.1.10 Statistical Analysis (Pearson Correlation)

SAS software was used to analyze the correlation between lignin properties (**APPENDIX A**) and measured properties of lignin-based PU flexible foams. Among the tested properties, a positive correlation was observed between density and the total hydroxyl (OH) content of lignin. Similarly, CFD was positively correlated with the total hydroxyl (OH) value of lignin. Ultimate elongation is negatively correlated to the total OH content of lignin, as summarized in (Table 8). This is because higher hydroxyl value lignin will tend to form more crosslink structure, which indirectly means forming more cell walls, and hence density and CFD will increase. On the contrary, this higher crosslink will make the foam stiff, decreasing the ultimate elongation values.

Table 8: Summary of Pearson Correlation Matrix

Pearson Correlation Coefficient	Total OH value of lignin	P-value
Density	0.68	<0.0001
CFD	0.69	<0.0001
Ultimate Elongation	-0.73	<0.0001

CHAPTER 4

CONCLUSIONS AND FUTURE WORKS

4.1 CONCLUSIONS

In this study, lignin-based flexible polyurethane foam was synthesized by partially substituting (20 wt%) of the petroleum-based polyols with thirteen different unmodified lignins (without any pretreatment or modification). Lignin incorporation improved the mechanical properties of the foams, such as compression force deflection (CFD), compression modulus, tear resistance, and support factor. Lignin addition increased the tensile strength of the foam and decreased the ultimate elongation. All the lignin-based foams were more thermally stable than control foam (without lignin). The Pearson Correlation analysis of lignin properties and performance of lignin-based PU flexible foams showed that total hydroxyl value was the most important lignin properties affecting the performance of lignin-based flexible PU foams. It was seen that foam properties such as density and compression force deflection were positively correlated to lignin's total hydroxyl content, while ultimate elongation was negatively correlated with the lignin's total hydroxyl content. Overall, among tested lignins, organosolv lignins proved to be more suitable for partially replacing fossil fuel-based polyol in PU flexible foam formulations intended for automotive applications. This is due to the fact that organosolv lignins have high solubility in co-polyol used for foam formulation, have lower sulfur content, lower T_g, and, most importantly, lower hydroxyl value.

4.2 FUTURE WORK

This study focused on evaluating the suitability of a wide range of lignins in replacing 20 wt% of petroleum-based polyol in the flexible PU foam formulation for the automotive industry. For considering lignin-based foam for automotive applications, it would be appropriate to perform additional tests such as the fogging number, odor, flammability, sound absorption, humidity, and aging properties of these foams. Lignin is a complex molecule and very challenging to work with, thus modeling the correlation between lignin properties and performance of the lignin-based foam would help identify which lignin properties can affect its performance the most. Partial least square regression (PLSR) modeling is a great tool, as it can tolerate highly correlated variables (lignin properties). The developed PLSR model will help predict the suitability of a new lignin sample for PU flexible foam application based on the lab's measured lignin properties. The group's future work will focus on using the most suitable lignins identified in this study and formulate foams with higher lignin content (30-50 wt%) while ensuring that developed foams still meet the required performance for automotive applications.

APPENDIX

APPENDIX A

Lignin Characteristics

Table A. 1: ^{31}P-NMR data

Lignin	Aliphatic (mmol/g)	Syringyl (mmol/g)	Condensed phenolic (mmol/g)	Guaiacyl (mmol/g)	Hydroxyphenyl (mmol/g)	COOH (mmol/g)	Total OH (mmol/g)
1-K-SW	1.99	0.00	1.10	1.85	0.25	0.43	5.62
2-O-HW	1.42	1.47	0.42	0.76	0.17	0.32	4.57
3-O-CS	2.25	0.35	0.12	0.52	0.13	0.53	3.90
4-K-SW	2.03	0.00	0.95	2.18	0.29	0.48	5.92
5-O-PS	1.33	0.20	0.13	1.31	0.21	0.22	3.40
6-K-SW	1.89	0.00	1.06	2.18	0.18	0.41	5.71
7-K-SW	1.77	0.00	0.84	2.06	0.26	0.43	5.36
8-O-HW	0.80	1.62	0.77	0.54	0.10	0.26	4.09
10-K-SW	1.76	0.00	1.43	2.67	0.29	0.56	6.71
11-K-BA	3.60	0.25	0.00	0.00	0.24	0.54	4.85
12-K-SW	2.35	0.00	1.22	2.27	0.21	0.37	6.42
13-K-SW	1.79	0.00	0.92	1.79	0.15	0.58	5.23
9-L-SW	0.98	0.00	0.09	0.06	0.01	0.02	1.16

Table A. 2: Ash Content, elemental analysis organic content, and Nitrogen

Lignin	Ash Content	C (wt%)	H (wt%)	N (wt%)
1-K-SW	4.34	62.5	5.86	0.67
2-O-HW	0.13	65.4	5.91	0.17
3-O-CS	3.28	60.9	6.31	2.36
4-K-SW	0.60	62.9	5.95	0.15
5-O-PS	1.02	63.9	6.56	1.74
6-K-SW	0.54	62.7	6.01	0.13
7-K-SW	0.65	62.9	5.99	0.14
8-O-HW	0.04	65.3	5.80	0.14
10-K-SW	1.92	62.3	5.60	0.12
11-K-BA	27.13	35.5	4.65	0.17
12-K-SW	0.78	63.7	6.02	0.10
13-K-SW	0.34	-	-	0.14
9-L-SW	11.45	42.4	5.16	0.19

Table A. 3: Elemental analysis, inorganic content

Lignin	S (wt%)	P (wt%)	K (wt%)	Mg (wt%)	Ca (wt%)	Na (wt%)
1-K-SW	1.97	0.00	0.11	0.01	0.04	0.70
2-O-HW	0.02	0.00	0.01	0.00	0.01	0.01
3-O-CS	1.03	0.07	1.19	0.11	0.16	0.02
4-K-SW	1.87	0.00	0.02	0.01	0.01	0.14
5-O-PS	1.08	0.03	0.14	0.01	0.01	0.09
6-K-SW	2.12	0.01	0.01	0.02	0.03	0.10
7-K-SW	1.57	0.00	0.02	0.01	0.01	0.19
8-O-HW	0.02	0.00	0.01	0.00	0.02	0.01
10-K-SW	2.81	0.00	0.12	0.00	0.01	0.69
11-K-BA	0.05	0.02	0.14	0.02	0.04	8.62
12-K-SW	1.80	0.00	0.02	0.01	0.01	0.20
13-K-SW	1.80	0.01	0.02	0.01	0.04	0.09
9-L-SW	5.85	0.01	0.23	0.17	3.99	0.17

Table A. 4: Elemental analysis, metal and metalloid

Lignin	B (ppm)	Zn (ppm)	Mn (ppm)	Fe (ppm)	Cu (ppm)	Al (ppm)
1-K-SW	21	17	40	46	1	159
2-O-HW	3	4	7	25	1	3
3-O-CS	8	50	23	611	95	10
4-K-SW	28	11	39	61	3	57
5-O-PS	11	43	20	2018	21	14
6-K-SW	9	5	28	33	3	70
7-K-SW	30	9	13	32	1	41
8-O-HW	1	3	2	13	4	10
10-K-SW	21	113	19	106	226	149
11-K-BA	138	9	44	38	5	246
12-K-SW	19	4	42	19	1	22
13-K-SW	4	2	7	28	2	71
9-L-SW	6	11	139	66	6	43

Table A. 5: Molecular weight of Lignin

Lignin	Mn (g/mol)	Mw (g/mol)	PDI
1-K-SW	1991	6582	3.30
2-O-HW	1285	3436	2.67
3-O-CS	1746	6245	3.57
4-K-SW	1773	6072	3.43
5-O-PS	1638	9079	5.53
6-K-SW	2031	8086	3.98
7-K-SW	1745	5514	3.16
8-O-HW	1640	4066	2.48
10-K-SW	2082	6921	3.32
11-K-BA	2008	6553	3.26
12-K-SW	1540	4288	2.79
13-K-SW	2247	12100	5.39
9-L-SW	400	5600	14.3

Table A. 6: Glass transition temperature of lignin

Lignin	Tg1 (°C)	Tg2 (°C)
1-K-SW	130.44	149.20
2-O-HW	104.29	-
9-L-SW	148.98	176.50
3-O-CS	142.81	-
10-K-SW	133.80	152.00
4-K-SW	135.46	147.76
11-K-BA	147.21	-
5-O-PS	95.82	-
6-K-SW	133.84	165.71
7-K-SW	138.62	154.55
12-K-SW	132.16	148.10
8-O-HW	133.57	-
13-K-SW	141.00	158.17

REFERENCES

REFERENCES

[1] M. F. Sonnenschein, *Polyurethanes: Science, Technology, Markets, and Trends*. 2014.

[2] R. B. Seymour *et al.*, “Otto Bayer Father of Polyurethanes,” in *Pioneers in Polymer Science*, Springer Netherlands, 1989, pp. 213–219.

[3] G. Woods, *The ICI Polyurethanes Book, second edition*. 1990.

[4] M. F. Sonnenschein, *Polyurethanes: Science, Technology, Markets, and Trends*, vol. 9781118737835. Wiley Blackwell, 2014.

[5] D. Randall and S. Lee, *The polyurethanes book*. [Huntsman Polyurethanes], 2002.

[6] “Global Polyurethane Market (2019 to 2023) - Identify Growth Segments for Investment - ResearchAndMarkets.com | Business Wire.” [Online]. Available: https://www.businesswire.com/news/home/20200320005325/en/Global-Polyurethane-Market-2019-2023---Identify. [Accessed: 22-Jun-2020].

[7] J. Bernardini, P. Cinelli, I. Anguillesi, M.-B. Coltelli, and A. Lazzeri, “Flexible polyurethane foams green production employing lignin or oxypropylated lignin,” *Eur. Polym. J.*, vol. 64, pp. 147–156, Mar. 2015, doi: 10.1016/j.eurpolymj.2014.11.039.

[8] J. O. Akindoyo, M. D. H. Beg, S. Ghazali, M. R. Islam, N. Jeyaratnam, and A. R. Yuvaraj, “Polyurethane types, synthesis and applications – a review,” *RSC Adv.*, vol. 6, no. 115, pp. 114453–114482, 2016, doi: 10.1039/C6RA14525F.

[9] “Global Polyols Market 2018-2022 | 9% CAGR Projection Through 2022 | Technavio | Business Wire.” [Online]. Available: https://www.businesswire.com/news/home/20200115005018/en/Global-Polyols-Market-2018-2022-9-CAGR-Projection. [Accessed: 22-Jun-2020].

[10] “Polyurethane Foams Market Global Forecast to 2023 | MarketsandMarkets.” [Online]. Available: https://www.marketsandmarkets.com/Market-Reports/polyurethane-foams-market-1251.html. [Accessed: 26-Mar-2020].

[11] D. Spitzer, “Soft landing : The value of construction is forecast to continue growing , boosting industry Urethane Foam Manufacturing in the US About this Industry (IBIS world),” 2019.

[12] G. Woods, *Flexible Polyurethane Foams, Chemistry and Technology*. Springer Netherlands, 1982.

[13] E. SJÖSTRÖM, “Chapter 4 - LIGNIN,” in *Wood Chemistry (Second Edition)*, Second Edi., E. SJÖSTRÖM, Ed. San Diego: Academic Press, 1993, pp. 71–89.

[14] M. Alinejad *et al.*, “Lignin-Based Polyurethanes : Opportunities for and Adhesives,” *Polymers (Basel).*, vol. 11, no. 1202, 2019.

[15] J. D. Crowe *et al.*, “Identification of developmental stage and anatomical fraction contributions to cell wall recalcitrance in switchgrass,” *Biotechnol. Biofuels*, vol. 10, no. 1, p. 184, Jul. 2017, doi: 10.1186/s13068-017-0870-5.

[16] A. Duval and M. Lawoko, “A review on lignin-based polymeric, micro- and nano-structured materials,” *React. Funct. Polym.*, vol. 85, pp. 78–96, 2014, doi: 10.1016/j.reactfunctpolym.2014.09.017.

[17] G. L. F. Gellerstedt and E. G. Henriksson, “Lignins: Major sources, structure and properties,” in *Monomers, Polymers and Composites from Renewable Resources*, Elsevier Ltd, 2008, pp. 201–224.

[18] W. Boerjan, J. Ralph, and M. Baucher, “ L IGNIN B IOSYNTHESIS ,” *Annu. Rev. Plant Biol.*, vol. 54, no. 1, pp. 519–546, Jun. 2003, doi: 10.1146/annurev.arplant.54.031902.134938.

[19] B. Nanayakkara, M. Manley-Harris, I. D. Suckling, and L. A. Donaldson, “Quantitative chemical indicators to assess the gradation of compression wood,” *Holzforschung*, vol. 63, no. 4, pp. 431–439, Jul. 2009, doi: 10.1515/HF.2009.062.

[20] H. Lange, S. Decina, and C. Crestini, “Oxidative upgrade of lignin - Recent routes reviewed,” in *European Polymer Journal*, 2013, vol. 49, no. 6, pp. 1151–1173, doi: 10.1016/j.eurpolymj.2013.03.002.

[21] C. Crestini, M. Crucianelli, M. Orlandi, and R. Saladino, “Oxidative strategies in lignin chemistry: A new environmental friendly approach for the functionalisation of lignin and lignocellulosic fibers,” *Catal. Today*, vol. 156, no. 1–2, pp. 8–22, Oct. 2010, doi: 10.1016/j.cattod.2010.03.057.

[22] A. Tejado, C. Peña, J. Labidi, J. M. Echeverria, and I. Mondragon, “Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis,” *Bioresour. Technol.*, 2007, doi: 10.1016/j.biortech.2006.05.042.

[23] D. Mohan, C. U. Pittman, and P. H. Steele, “Single, binary and multi-component adsorption of copper and cadmium from aqueous solutions on Kraft lignin-a biosorbent,” *J. Colloid Interface Sci.*, 2006, doi: 10.1016/j.jcis.2005.11.023.

[24] F. S. Chakar and A. J. Ragauskas, “Review of current and future softwood kraft lignin process chemistry,” in *Industrial Crops and Products*, 2004, doi: 10.1016/j.indcrop.2004.04.016.

[25] N. E. El Mansouri and J. Salvadó, “Structural characterization of technical lignins for the production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins,” *Ind. Crops Prod.*, 2006, doi: 10.1016/j.indcrop.2005.10.002.

[26] H. Yoshida and H. Hatakeyama, “Fractionation of kraft lignin by successive extraction with organic solvents. 1. Functional groups (13)C-NMR-spectra and molecular weight distributions,” *Holzforsch. (Germany, F.R.)*, 1986.

[27] J. Gullichsen, H. Paulapuro, and C.-J. Fogelholm, “Papermaking Science and Technology, Book 6B.Chemical Pulping.” Fapet Oy, 2000.

[28] F. Xu, J. X. Sun, R. Sun, P. Fowler, and M. S. Baird, “Comparative study of organosolv lignins from wheat straw,” *Ind. Crops Prod.*, vol. 23, no. 2, pp. 180–193, Mar. 2006, doi: 10.1016/j.indcrop.2005.05.008.

[29] D. D. Laskar, B. Yang, H. Wang, and J. Lee, “Pathways for biomass-derived lignin to hydrocarbon fuels,” *Biofuels, Bioprod. Biorefining*, vol. 7, no. 5, pp. 602–626, Sep. 2013, doi: 10.1002/bbb.1422.

[30] N. E. El Mansouri and J. Salvadó, “Structural characterization of technical lignins for the production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins,” *Ind. Crops Prod.*, vol. 24, no. 1, pp. 8–16, Jul. 2006, doi: 10.1016/j.indcrop.2005.10.002.

[31] J. H. Lora, “Industrial commercial lignins: Sources, properties and applications,” in *Monomers, Polymers and Composites from Renewable Resources*, Elsevier Ltd, 2008, pp. 225–241.

[32] J. FAN and H. ZHAN, “Optimization of Synthesis of Spherical Lignosulphonate Resin and Its Structure Characterization* * Supported by the Ph.D. Programs Foundation of Ministry of Education of China (20020561001).,” *Chinese J. Chem. Eng.*, vol. 16, no. 3, pp. 407–410, Jun. 2008, doi: 10.1016/S1004-9541(08)60097-X.

[33] M. N. Belgacem and A. Gandini, *Monomers , Polymers and Composites*. .

[34] D. Areskogh, J. Li, G. Gellerstedt, and G. Henriksson, “Investigation of the molecular weight increase of commercial lignosulfonates by laccase catalysis,” *Biomacromolecules*, 2010, doi: 10.1021/bm901258v.

[35] P. Cinelli, I. Anguillesi, and A. Lazzeri, “Green synthesis of flexible polyurethane foams from liquefied lignin,” *Eur. Polym. J.*, vol. 49, no. 6, pp. 1174–1184, Jun. 2013, doi: 10.1016/j.eurpolymj.2013.04.005.

[36] H. Pawlik and A. Prociak, “Influence of Palm Oil-Based Polyol on the Properties of Flexible Polyurethane Foams,” *J. Polym. Environ.*, vol. 20, no. 2, pp. 438–445, Jun. 2012, doi: 10.1007/s10924-011-0393-2.

[37] N. Z. K. S. O. T. L. and S. AHMAD*, “EFFECT OF TRIETHANOLAMINE ON THE PROPERTIES OF PALM-BASED FLEXIBLE POLYURETHANE FOAMS,” 2004.

[38] A. Prociak, P. Rojek, and H. Pawlik, “Flexible polyurethane foams modified with natural oil based polyols,” *J. Cell. Plast.*, vol. 48, no. 6, pp. 489–499, Nov. 2012, doi:

10.1177/0021955X12446210.

[39] E. I. Victor[1], J. O. Okechukwu[2], M. A. Femi[2], and O. M. Ogbonneya[3], “Polyurethane Foam Production using Sunflower oil and Soybean oil as Polyol and Surfactant,” *Int. J. Mod. Sci. Technol.*, vol. 4, no. 2, pp. 48–53, 2019.

[40] Z. S. Petrovic, “Polyurethanes from vegetable oils,” *Polym. Rev.*, vol. 48, no. 1, pp. 109–155, Jan. 2008, doi: 10.1080/15583720701834224.

[41] C. Sharma, S. Kumar, A. R. Unni, V. K. Aswal, S. K. Rath, and G. Harikrishnan, “Foam stability and polymer phase morphology of flexible polyurethane foams synthesized from castor oil,” *J. Appl. Polym. Sci.*, vol. 131, no. 17, p. n/a-n/a, Sep. 2014, doi: 10.1002/app.40668.

[42] D. P. Pfister, Y. Xia, and R. C. Larock, “Recent Advances in Vegetable Oil-Based Polyurethanes,” *ChemSusChem*, vol. 4, no. 6, pp. 703–717, Jun. 2011, doi: 10.1002/cssc.201000378.

[43] R. Gu and M. M. Sain, “Effects of Wood Fiber and Microclay on the Performance of Soy Based Polyurethane Foams,” *J. Polym. Environ.*, vol. 21, no. 1, pp. 30–38, Nov. 2013, doi: 10.1007/s10924-012-0538-y.

[44] H. R. Zhang, H. Pang, L. Zhang, X. Chen, and B. Liao, “Biodegradability of Polyurethane Foam from Liquefied Wood Based Polyols,” *J. Polym. Environ.*, vol. 21, no. 2, pp. 329–334, Nov. 2013, doi: 10.1007/s10924-012-0542-2.

[45] R. C. S. Araújo, V. M. D. Pasa, and B. N. Melo, “Effects of biopitch on the properties of flexible polyurethane foams,” *Eur. Polym. J.*, vol. 41, no. 6, pp. 1420–1428, Jun. 2005, doi: 10.1016/j.eurpolymj.2004.12.021.

[46] S. M. Notley and M. Norgren, “Surface energy and wettability of spin-coated thin films of lignin isolated from wood,” *Langmuir*, vol. 26, no. 8, pp. 5484–5490, Apr. 2010, doi: 10.1021/la1003337.

[47] F. Bertini, M. Canetti, A. Cacciamani, G. Elegir, M. Orlandi, and L. Zoia, “Effect of ligno-derivatives on thermal properties and degradation behavior of poly(3-hydroxybutyrate)-based biocomposites,” *Polym. Degrad. Stab.*, vol. 97, no. 10, pp. 1979–1987, 2012, doi: 10.1016/j.polymdegradstab.2012.03.009.

[48] “Modification of Water Sorption Capacity of Polydimethylsiloxane based Composites by Incorporation of Lignin | Request PDF.” [Online]. Available: https://www.researchgate.net/publication/281945008_Modification_of_Water_Sorption_Capacity_of_Polydimethylsiloxane_based_Composites_by_Incorporation_of_Lignin. [Accessed: 10-Apr-2020].

[49] “Lignin: Technology, Applications and Markets Special Market Analysis Study,” 2016.

[50] S. Wang, W. Liu, D. Yang, and X. Qiu, “Highly Resilient Lignin-Containing Polyurethane

Foam," doi: 10.1021/acs.iecr.8b05072.

[51] L. Rozite, J. Varna, R. Joffe, and A. Pupurs, "Nonlinear behavior of PLA and lignin-based flax composites subjected to tensile loading," *J. Thermoplast. Compos. Mater.*, vol. 26, no. 4, pp. 476–496, May 2013, doi: 10.1177/0892705711425846.

[52] F. Le Digabel and L. Avérous, "Effects of lignin content on the properties of lignocellulose-based biocomposites," *Carbohydr. Polym.*, vol. 66, no. 4, pp. 537–545, Nov. 2006, doi: 10.1016/j.carbpol.2006.04.023.

[53] H. Wang, J. Zou, Y. Shen, G. Fei, and J. Mou, "Preparation and colloidal properties of an aqueous acetic acid lignin containing polyurethane surfactant," *J. Appl. Polym. Sci.*, vol. 130, no. 3, pp. 1855–1862, Nov. 2013, doi: 10.1002/app.39300.

[54] F. A. Faria *et al.*, "Lignin-based polyurethane doped with carbon nanotubes for sensor applications," *Polym. Int.*, vol. 61, no. 5, pp. 788–794, May 2012, doi: 10.1002/pi.4140.

[55] C. S. Carriço, T. Fraga, and V. M. D. Pasa, "Production and characterization of polyurethane foams from a simple mixture of castor oil, crude glycerol and untreated lignin as bio-based polyols," *Eur. Polym. J.*, vol. 85, pp. 53–61, Dec. 2016, doi: 10.1016/j.eurpolymj.2016.10.012.

[56] S. Gómez-Fernández, L. Ugarte, T. Calvo-Correas, C. Peña-Rodríguez, M. A. Corcuera, and A. Eceiza, "Properties of flexible polyurethane foams containing isocyanate functionalized kraft lignin," *Ind. Crops Prod.*, vol. 100, pp. 51–64, Jun. 2017, doi: 10.1016/j.indcrop.2017.02.005.

[57] P. Cinelli, I. Anguillesi, and A. Lazzeri, "Green synthesis of flexible polyurethane foams from liquefied lignin," *Eur. Polym. J.*, vol. 49, no. 6, pp. 1174–1184, 2013, doi: 10.1016/j.eurpolymj.2013.04.005.

[58] H. Jeong, J. Park, S. Kim, J. Lee, and N. Ahn, "Compressive viscoelastic properties of softwood kraft lignin-based flexible polyurethane foams," *Fibers Polym.*, vol. 14, no. 8, pp. 1301–1310, Aug. 2013, doi: 10.1007/s12221-013-1301-2.

[59] J. Bernardini, I. Anguillesi, M.-B. Coltelli, P. Cinelli, and A. Lazzeri, "Optimizing the lignin based synthesis of flexible polyurethane foams employing reactive liquefying agents," *Polym. Int.*, vol. 64, no. 9, pp. 1235–1244, Sep. 2015, doi: 10.1002/pi.4905.

[60] K. Wysocka, K. Szymona, A. G. McDonald, and M. Maminski, "Characterization of thermal and mechanical properties of lignosulfonate- and hydrolyzed lignosulfonate-based polyurethane foams," *BioResources*, vol. 11, no. 3, pp. 7355–7364, 2016, doi: 10.15376/biores.11.3.7355-7364.

[61] S. R. Yearla and K. Padmasree, "Preparation and characterisation of lignin nanoparticles: evaluation of their potential as antioxidants and UV protectants," *J. Exp. Nanosci.*, vol. 11, no. 4, pp. 289–302, Mar. 2016, doi: 10.1080/17458080.2015.1055842.

[62] N. Mandlekar *et al.*, "An Overview on the Use of Lignin and Its Derivatives in Fire Retardant Polymer Systems," in *Lignin - Trends and Applications*, InTech, 2018.

[63] A. Cayla, F. Rault, S. Giraud, F. Salaün, V. Fierro, and A. Celzard, "PLA with Intumescent System Containing Lignin and Ammonium Polyphosphate for Flame Retardant Textile," *Polymers (Basel).*, vol. 8, no. 9, p. 331, Sep. 2016, doi: 10.3390/polym8090331.

[64] A. Lee and Y. Deng, "Green polyurethane from lignin and soybean oil through non-isocyanate reactions," *Eur. Polym. J.*, vol. 63, pp. 67–73, Feb. 2015, doi: 10.1016/j.eurpolymj.2014.11.023.

[65] H. Chung and N. R. Washburn, "Improved lignin polyurethane properties with lewis acid treatment," *ACS Appl. Mater. Interfaces*, vol. 4, no. 6, pp. 2840–2846, 2012, doi: 10.1021/am300425x.

[66] E. Delebecq, J. P. Pascault, B. Boutevin, and F. Ganachaud, "On the versatility of urethane/urea bonds: Reversibility, blocked isocyanate, and non-isocyanate polyurethane," *Chemical Reviews*, vol. 113, no. 1. American Chemical Society, pp. 80–118, 09-Jan-2013, doi: 10.1021/cr300195n.

[67] "Biodegradable and Biobased Polymers for Environmental and Biomedical Applications | Wiley." [Online]. Available: https://www.wiley.com/en-us/Biodegradable+and+Biobased+Polymers+for+Environmental+and+Biomedical+Applications-p-9781119117339. [Accessed: 14-Jul-2020].

[68] G. I.-T. Journal and undefined 1984, "The glass transitions of lignin and hemicellulose and their measurement by differential thermal analysis," *pascal-francis.inist.fr*.

[69] D. A. I. Goring, "Thermal softening of lignin, hemicellulose and cellulose," 1963.

[70] "Lignin," in *Thermal Properties of Green Polymers and Biocomposites*, Dordrecht: Kluwer Academic Publishers, pp. 171–215.

[71] T. Nguyen, E. Zavarin, and E. M. Barrall, "Thermal Analysis of Lignocellulosic Materials. Part I. Unmodified Materials," *J. Macromol. Sci. Part C*, vol. 20, no. 1, pp. 1–65, Jan. 1981, doi: 10.1080/00222358108080014.

[72] PerkinElmer and Inc, "Investigation Into the Tg of Forms."

[73] R. W. Thring, M. N. Vanderlaan, and S. L. Griffin, "Polyurethanes from Alcell® lignin," *Biomass and Bioenergy*, vol. 13, no. 3, pp. 125–132, Jan. 1997, doi: 10.1016/S0961-9534(97)00030-5.

[74] A. Vishtal and A. Kraslawski, "Challenges in industrial applications of technical lignins," *BioResources*, vol. 6, no. 3, pp. 3547–3568, 2011, doi: 10.15376.

[75] X. Huang, C. F. De Hoop, J. Xie, C. Y. Hse, J. Qi, and T. Hu, "Characterization of

Biobased Polyurethane Foams Employing Lignin Fractionated from Microwave Liquefied Switchgrass," *Int. J. Polym. Sci.*, vol. 2017, 2017, doi: 10.1155/2017/4207367.

[76] X. Luo, A. Mohanty, and M. Misra, "Lignin as a reactive reinforcing filler for water-blown rigid biofoam composites from soy oil-based polyurethane," *Ind. Crops Prod.*, vol. 47, pp. 13–19, May 2013, doi: 10.1016/j.indcrop.2013.01.040.

[77] O. S. H. Santos, M. Coelho da Silva, V. R. Silva, W. N. Mussel, and M. I. Yoshida, "Polyurethane foam impregnated with lignin as a filler for the removal of crude oil from contaminated water.," *J. Hazard. Mater.*, vol. 324, no. Pt B, pp. 406–413, Feb. 2017, doi: 10.1016/j.jhazmat.2016.11.004.

[78] R. W. Thring, P. Ni, and S. M. Aharoni, "MOLECULAR WEIGHT EFFECTS OF THE SOFT SEGMENT ON THE ULTIMATE PROPERTIES OF LIGNIN-DERIVED POLYURETHANES," *Int. J. Polym. Mater.*, vol. 53, no. 6, pp. 507–524, Jun. 2004, doi: 10.1080/00914030490267627.

[79] K. Wysocka, K. Szymona, A. G. McDonald, and M. Ł. Mamiński, "Characterization of Thermal and Mechanical Properties of Lignosulfonate- and Hydrolyzed Lignosulfonate-based Polyurethane Foams," *BioResources*, vol. 11, no. 3, Jul. 2016, doi: 10.15376/biores.11.3.7355-7364.

[80] H. Yoshida, R. Mörck, K. P. Kringstad, and H. Hatakeyama, "Kraft lignin in polyurethanes I. Mechanical properties of polyurethanes from a kraft lignin–polyether triol–polymeric MDI system," *J. Appl. Polym. Sci.*, vol. 34, no. 3, pp. 1187–1198, Aug. 1987, doi: 10.1002/app.1987.070340326.

[81] R. J. Zdrahala, R. M. Gerkin, S. L. Hager, and F. E. Critchfield, "Polyether-based thermoplastic polyurethanes. I. Effect of the hard-segment content," *J. Appl. Polym. Sci.*, vol. 24, no. 9, pp. 2041–2050, Nov. 1979, doi: 10.1002/app.1979.070240912.

[82] L. W. Hill, "Calculation of crosslink density in short chain networks," *Prog. Org. Coatings*, vol. 31, no. 3, pp. 235–243, Nov. 1997, doi: 10.1016/S0300-9440(97)00081-7.

[83] J. Bernardini, I. Anguillesi, M. B. Coltelli, P. Cinelli, and A. Lazzeri, "Optimizing the lignin based synthesis of flexible polyurethane foams employing reactive liquefying agents," *Polym. Int.*, vol. 64, no. 9, pp. 1235–1244, Sep. 2015, doi: 10.1002/pi.4905.

[84] A. Kržan and M. Kunaver, "Microwave heating in wood liquefaction," *J. Appl. Polym. Sci.*, vol. 101, no. 2, pp. 1051–1056, Jul. 2006, doi: 10.1002/app.23488.

[85] J. Xie, J. Qi, C.-Y. Hse, and T. F. Shupe, "Effect of Lignin Derivatives in the Bio-Polyols from Microwave Liquefied Bamboo on the Properties of Polyurethane Foams," *BioResources*, vol. 9, no. 1, Dec. 2013, doi: 10.15376/biores.9.1.578-588.

[86] Z. Zheng, "Rapid Liquefaction of Wood in Polyhydric Alcohols Under Microwave Heating and its Liquefied Products for Preparation of Rigid Polyurethane Foam," *Open Mater. Sci. J.*, vol. 5, no. 1, pp. 1–8, May 2011, doi: 10.2174/1874088X01105010001.

[87] P. Cinelli, I. Anguillesi, and A. Lazzeri, “Green synthesis of flexible polyurethane foams from liquefied lignin,” in *European Polymer Journal*, 2013, vol. 49, no. 6, pp. 1174–1184, doi: 10.1016/j.eurpolymj.2013.04.005.

[88] C. A. Cateto, M. F. Barreiro, A. E. Rodrigues, and M. N. Belgacem, “Kinetic study of the formation of lignin-based polyurethanes in bulk,” *React. Funct. Polym.*, vol. 71, no. 8, pp. 863–869, Aug. 2011, doi: 10.1016/J.REACTFUNCTPOLYM.2011.05.007.

[89] G. Gellerstedt, “Gel Permeation Chromatography,” Springer, Berlin, Heidelberg, 1992, pp. 487–497.

[90] J. Sameni, S. Krigstin, and M. Sain, “Acetylation & lignin solubility,” 2017.

[91] T. Elastomers, “Standard Test Methods for Flexible Cellular Materials — Slab , Bonded , and Molded Urethane Foams,” *Astm*, vol. Designatio, pp. 1–29, 2012, doi: 10.1520/D3574-11.2.

[92] A. Lee and Y. Deng, “Green polyurethane from lignin and soybean oil through non-isocyanate reactions,” *Eur. Polym. J.*, vol. 63, pp. 67–73, Feb. 2015, doi: 10.1016/j.eurpolymj.2014.11.023.

[93] H. Chung and N. R. Washburn, “Improved lignin polyurethane properties with lewis acid treatment,” *ACS Appl. Mater. Interfaces*, vol. 4, no. 6, pp. 2840–2846, Jun. 2012, doi: 10.1021/am300425x.

[94] S. Burattini *et al.*, “A healable supramolecular polymer blend based on aromatic π-π Stacking and hydrogen-bonding interactions,” *J. Am. Chem. Soc.*, vol. 132, no. 34, pp. 12051–12058, Sep. 2010, doi: 10.1021/ja104446r.

[95] S. M. Kang, S. J. Lee, and B. K. Kim, “Shape memory polyurethane foams,” *Express Polym. Lett.*, vol. 6, no. 1, pp. 63–69, Jan. 2012, doi: 10.3144/expresspolymlett.2012.7.

[96] I. Javni, Z. S. Petrović, A. Guo, and R. Fuller, “Thermal stability of polyurethanes based on vegetable oils,” *J. Appl. Polym. Sci.*, vol. 77, no. 8, pp. 1723–1734, Aug. 2000, doi: 10.1002/1097-4628(20000822)77:8<1723::AID-APP9>3.0.CO;2-K.

[97] E. Hablot, D. Zheng, M. Bouquey, and L. Avérous, “Polyurethanes based on castor oil: Kinetics, chemical, mechanical and thermal properties,” *Macromol. Mater. Eng.*, vol. 293, no. 11, pp. 922–929, Nov. 2008, doi: 10.1002/mame.200800185.