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Application of Lignins in Formulation and Manufacturing Bio-Based Polyurethanes by ^{31}P NMR Spectroscopy

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Additional information is available at the end of the chapter

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Abstract

The application of several industrial and technical biomass lignins from forestry and agricultural residues extracted by different chemical pulping processes in view of bio-based polyurethanes were studied. Several qualitative and quantitative methods were utilized to characterize and elucidate lignin profiles by evaluating their physical and chemical properties as a potential substitute for petroleum-based polyols. The morphology, molecular weight distributions, elemental compositions, glass transition temperature and several important functional groups containing hydroxyl units were classified and their contents were determined quantitatively. In this chapter, lignin substitution in polyurethane by (i) direct substitution, (ii) with combination of polyols or (iii) chemically modified was reviewed. The emerging information aims at addressing a number of pressing issues relevant to the scientific development for value-added applications from lignins during industrial production of biofoams.

Keywords: lignins, characterization, polyols, chemical modification, polyurethane

1. Introduction

Polymers play an essential and ubiquitous role in our daily lives due to their extraordinary wide variety of both physical and chemical properties [1]. However, with ever increasing global concern over rapid depletion of non-renewable fossil fuel-based resources, uncertainties of petroleum prices and the high energy intensity in production of chemicals and synthetic polymers, there is a strong interest worldwide in developing suitable technologies

that can derive chemicals and materials from renewable biomass [2]. In recent years, the conversion of renewable lignocellulosic resources into chemicals, liquids fuels and feed supplement has gained considerable attention. Modification and characterization of bio-based polymers for preparation of higher valued green chemicals and bio-based products favors the future use of lignin biomass components with substantial environmental and economical benefits [3–6].

Lignin is the second most naturally abundant biopolymer substance in plant cell walls, exceeded only by cellulose [7, 8]. Its main function is to impart rigidity to the cell walls and, acting as an intercellular binder, impart to woods resistance to compression, impact and bending.

Lignin is an amorphous, highly branched polyphenolic macromolecule of complex structure with high molecular weight. The chemical structure of lignin is highly irregular and extremely challenging. Lignin polymer consists primarily of phenyl propanoid units mainly *p*-coumaryl alcohol (H), coniferyl alcohol (G) and/or sinapyl alcohol (S). These components are cross-linked together in three dimensions via a radical coupling process during its biosynthesis [9–15]. Its physical and chemical properties are highly dependent on the wood species, botanic region and the isolation processes [16, 17] (Figure 1).

Lignin is available in large quantities as a byproduct of the pulp and paper and hydrolytic industries. The most abundant industrial lignins are from kraft and sulfite pulping processes. Lignins obtained under these processes undergo significant structural changes and are no longer identical to their original native structures [10, 18–20]. Due to its complex nature and undefined chemical structure, the industrial applications of lignin are rather limited. Lignin is utilized almost exclusively as fuel to power the evaporators of the chemical recovery processes and liquor concentration system of pulp mills [21]. However, based on its interesting functionalities and properties, lignin offers perspective for higher added value applications in renewable products [22].

The overall reactivity of different lignins depends on their chemical structures [23]. The lignin polymer contains a large number of several important functional groups [24] including

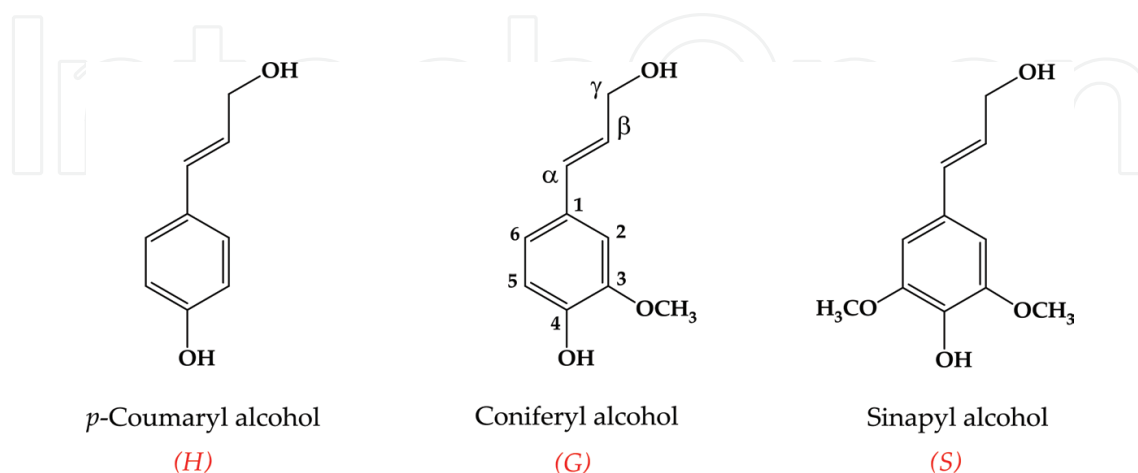


Figure 1. Chemical structure of lignin monomeric phenylpropanoid units.

phenolic hydroxyl, aliphatic hydroxyl and carboxylic acid groups. Different lignin samples contain different types and quantities of these functional groups that could be utilized in making and/or replacing a majority of petroleum-based products in the manufacturing of industrial biomaterials and bio-composites [25–27] such as polyurethanes [28–30]. Traditional polyurethane foam is made from petroleum-based polyols that biodegrades slowly if at all. The main advantage of lignin polymer group lies, on one hand, in the sustainability of renewable raw materials and on the other hand in the 'zero waste' principle resulting from their bio-degradability.

Polyurethanes (PU) are considered as one of the most useful multi-purpose polymers with formulations covering a wide range of products and applications. PU can be utilized as sheets, foams or paints in various products such as flexible foam seating, rigid foam insulating panels, high performance adhesives and sealants [31].

PU polymers are formed through step-growth polymerization by reacting a monomer which has two or more isocyanate functional groups with another monomer containing two or more hydroxyl groups in the presence of a catalyst [32].

The first monomeric unit, isocyanates are classified as aromatic or aliphatic. Aromatic diisocyanates such as toluene diisocyanate (TDI) and methylene diphenyl diisocyanates (MDI) are mostly utilized in formation of polyurethanes since the aromatically linked isocyanate group is much more reactive than the aliphatic one. In addition, the aromatic isocyanate is more economical. However, the aliphatic isocyanates such as hexamethylene diisocyanates (HDI) and isophorone diisocyanates (IPDI) are used only if special properties are required for the final product [33–36].

Polyols, the other monomeric component, are classified as polyether or polyester polyols. Polyols can be further classified according to their end use as flexible or rigid, depending on the functionality of the initiator and their molecular weight. Flexible polyols have molecular weights ranging from 2000 to 10,000 containing 18–56 hydroxyl units while rigid polyols have molecular weights ranging from 250 to 700 with 300–700 hydroxyl units. Polyols with 700–2000 molecular weights and 60–280 hydroxyl units are used to improve stiffness or flexibility to base system [33–36].

Lignin contains considerable amount of aliphatic hydroxyl groups on the propionic side chain of its several different monomeric units. These units contain both primary and secondary hydroxyl groups with properties similar to polyols. However, unlike petroleum polyols, these propionic hydroxyl groups are not the major factor for order of lignin reactivity. Other lignin features attribute and influence lignin performance in PU formulation.

Many polymer properties such as T_g, modulus, tensile strength, etc. are directly dependent upon their molecular weights. Molecular weight determinations on a variety of isolated lignins would provide essential information on the molecular size or size distribution of different polymeric fragments in lignin and their physical and chemical properties during copolymerization [37]. The lignin properties are related not only to the nature of the hydrophilic groups, which depends upon the pulping process, but also to the size of the polymeric

pieces, which in turn depends on the recovery techniques used to process the black liquors. The molecular weight for a number of lignin will help to identify the most suitable lignin(s) for a PU application.

Lignins extracted under different processes contain different chemical and physical properties. Therefore, in order to increase the reactivity of lignin and improve their compatibilities with other polymers, certain functional groups may be selectively modified. For example, free phenolic-OH groups are found to be more reactive [38, 39] than benzylic-OH except toward diisocyanates [40, 41]. In this case, the reaction of lignin with alkene oxide would result in the formation of lignin-polyol derivatives, which in turn improve the solubility, and uniformity of lignin [39, 42, 43]. Modification of specific functional group(s) may be performed in accordance to the results obtained from polyurethane polymerization using lignin. Characterization, selection and modification of lignin polymer as raw materials would then pave the way to prepare a bio-based polymer with similar characteristics to polyols that could be utilized in substituting polyols for industrial applications during the polyurethane production.

In this chapter, physical and chemical properties such as functional groups, molecular weights and chemical modification of differently isolated lignins from agriculture residues and forestry were investigated for their potential as a substitute for polyols during polyurethane productions.

A number of industrial, technical and commercially available lignin samples were characterized by employing different qualitative and quantitative techniques [44, 45]. In these studies, different lignin samples were examined to elucidate their physical and chemical profiles in view of biomaterials applications. The L1 and L2 samples were hardwood lignins extracted by kraft and organosolv pulping processes, respectively. The subsequent four samples were all recovered from softwoods. The L3 and L4 were extracted by sulfite while L5 and L6 were isolated by kraft process. However, the L6 lignin sample was further modified with low sulfonated sodium salt. The L7 and L8 samples were soda lignin samples extracted from wheat straw. Detailed information regarding their suppliers, as well as their moisture and ash contents corresponding to each lignin sample, is reported in **Table 1**.

The experimental data show the L2 sample has the lowest, while the L4 and L6 have the highest moisture and ash content. This is not surprising since the L2 was extracted by organosolv process. The process is known to yield lignin which is hydrophobic and has the higher purity with lowest ash content among other lignin samples. Meanwhile, the L4 and L6 were isolated by sulfite process where the resulting lignosulfonates are known to be hydrophilic lignin and prone to absorb moisture more readily. More specifically, in the case of L6, the percent moisture content was found to increase by more than twofolds from $3.70 \pm 0.09\%$ to $8.20 \pm 0.08\%$ during two and a half years of storage time. However, the most striking feature was its high concentration of inorganic contaminants. Repeated measurements showed that almost two thirds of L6 contains ash and non-organic materials. In general, the lignosulfonates and sulfonated kraft lignin were found to have the highest ash content.

Sample	Lignin source	Feedstock	Isolation process	Moisture (%)	Ash (%)
L1	Canadian Mill	Hardwoods	Kraft	6.05 ± 0.09	0.45 ± 0.04
L2	Aldrich, Catalog No. 371017	Hardwoods	Organosolv	2.40 ± 0.00	0.11 ± 0.01
L3	Tembec, Arbo SO1	Softwoods	Sulfite	4.66 ± 0.03	24.15 ± 0.27
L4	Aldrich, Catalog No. 471038 ^a	Softwoods	Sulfite	6.81 ± 0.04	20.02 ± 0.08
L5	Indulin AT, MeadWestvaco	Softwoods	Kraft	4.66 ± 0.12	3.06 ± 0.30
L6	Aldrich, Catalog No. 471003 ^b	Softwoods	Kraft, low sulfonated	3.70 ± 0.09	66.19 ± 0.18
L7	Protobind 2400, Green Value	Wheat straw	Soda	2.48 ± 0.07	1.12 ± 0.01
L8	Protobind 3000, Green Value	Wheat straw	Soda	6.45 ± 0.02	2.12 ± 0.03

^aModified sodium lignosulfonate.

^bSodium salt of low sulfonated kraft lignin.

Table 1. Specification of various types of lignin and their moisture and ash content [44, 45].

The elemental compositions for various types of lignins are exclusively different; the percent elemental composition for each lignin sample in terms of carbon, hydrogen, nitrogen, oxygen, sulfur and methoxy content and the empirical formulae and the molecular weight of each lignin per C₉ unit was reported in **Table 2** [44, 45]. The lignosulfonate samples have the lowest carbon, hydrogen and methoxy content followed by the sulfonated kraft lignin. The oxygen, sulfur and the molecular weights for these samples were found to be at the highest. This is somewhat to be expected since during the sulfite pulping process, the substituted sulfonate groups mostly at C_α and C_γ of lignin propanoic side-chains bear three oxygen atoms, leading to higher molecular weight. The organosolv lignin sample was found to contain the highest percentage of carbon and methoxy contents even when compared to its hardwood counterpart kraft lignin sample. Considering the monomeric units of both L1 and L2 samples that bear two methoxy groups, the L2 was found to have the lowest oxygen content with the lowest molecular weight among other lignins. Apart from lignosulfonates and sulfonated kraft lignin (L6), the sulfur content for kraft lignins (L1) and Indulin AT (L5) were found to be 1.93 and 1.32%, respectively. Determination of nitrogen content in lignin is also important since its quantity varies for different types of industrial lignins. The percent elemental nitrogen in order of descending was found for the L3, L7, L5 and L8 samples to be 1.09, 0.79, 0.59 and 0.31%, respectively. However, the nitrogen content was calculated in the order of L8, L3, L7 and L5 to contain 0.43, 0.22, 0.11 and 0.08 nitrogen element per C₉ unit, respectively.

Lignin sample	Elemental analysis						C9 structural unit	MW (g/mol)
	%C	%H	%N	%O	%S	%OCH ₃		
L1	58.12	6.18	<0.50	33.05	1.93	17.09	C ₉ H _{9.40} O _{3.18} S _{0.13} (OCH ₃) _{1.156}	208.37
L2	65.56	5.81	<0.50	27.65	<0.50	17.37	C ₉ H _{7.51} O _{2.15} (OCH ₃) _{1.028}	181.92
L3	40.99	4.65	1.09	37.26	6.63	6.74	C ₉ H _{11.16} O _{5.95} N _{0.22} S _{0.58} (OCH ₃) _{0.612}	255.23
L4	41.98	4.75	<0.50	39.71	6.59	7.96	C ₉ H _{10.96} O _{6.18} S _{0.57} (OCH ₃) _{0.713}	258.53
L5	58.86	6.24	0.59	30.82	1.32	11.72	C ₉ H _{10.06} O _{3.08} N _{0.08} S _{0.08} (OCH ₃) _{0.751}	194.67
L6	44.15	5.20	<0.50	38.08	4.16	8.77	C ₉ H _{11.44} O _{5.56} S _{0.34} (OCH ₃) _{0.750}	242.93
L7	61.55	6.32	0.79	29.44	1.19	17.21	C ₉ H _{9.07} O _{2.53} N _{0.11} S _{0.07} (OCH ₃) _{1.092}	195.54
L8	59.75	6.16	0.31	28.6	<0.50	11.2	C ₉ H _{9.81} O _{2.78} N _{0.43} (OCH ₃) _{0.704}	190.41

Table 2. Elemental analysis, OCH₃ content, empirical formulae and molecular weight per C₉ lignin unit for different types of lignin [44, 45].

2. Lignin substitution in PU formulations

Lignin incorporation in polyurethane production has been one of the most intensively investigated applications [26–30, 46–55]. Lignin utilization modifies the polyurethane cure rate by contributing aromatic groups and increasing the degree of cross-linking. Lignin acts as a reinforcing agent which adds rigidity to the polymeric matrix [29]. Several studies have suggested that i) the solubility and ii) the uniformity of the lignin are the foremost important key parameters affecting its reactivity for polyols substitution in polyurethane production [52, 46–58]. This in turn is directly dependent upon different classes of hydroxyl groups that may be present in lignin causing both electronic and steric factors affecting the lignin reactivity [59]. Lignin substitution in polyurethane could be achieved by either i) direct substitution, ii) with combination of polyols [37, 46, 47, 49] or iii) chemically modified [28, 60–62].

2.1. Direct lignin substitution

There are three major types of hydroxyl groups in lignin. They are phenolic hydroxyl, α -hydroxyl and γ -carbinol group. Generally, phenolic –OH units are the most acidic and reactive groups. They play an important role in alkali-catalyzed reactions. Under acidic conditions, α -hydroxyls are transformed into active benzylic carbon cation leading to a variety of addition or transformation reactions while phenolic γ -carbinol is released as formaldehyde under both acidic and alkaline conditions [63] (**Figure 2**).

Different lignin samples contain different types and content of phenolic hydroxyl units depending on the pulping and isolation processes [64, 65]. Lignin extracted under soda pulping is reported to contain less phenolic hydroxyl groups and higher condensed structures than kraft lignin [66]. On the other hand, kraft lignin, as compared to MWL, is suggested by

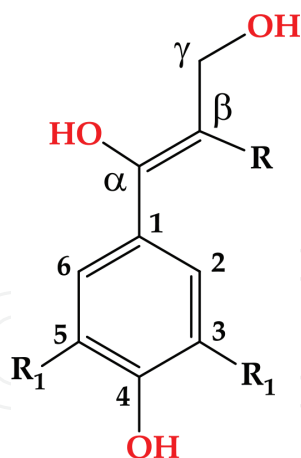


Figure 2. Three major types of hydroxyl groups in a monomeric structure in lignin.

Lai [63] to have higher content of phenolic hydroxyl group, α -carbonyl and stilbene structure with lower aliphatic hydroxyl group content. Steam explosion lignin and acid hydrolysis lignin have been suggested to be the most and the least compatible in preparation of polyurethane network films. Lignin isolated from other processes such as organosolv, kraft and MWL are reported to decrease in the order of their compatibility during polyurethane copolymerization [63]. Despite the extensive research on different types of lignins, there is limited information on utilization of soda lignin from agriculture residues in polyurethane application.

An important factor for incorporation of lignin in preparation of PU is the absolute determination of aliphatic $-\text{OH}$ groups for calculating the NCO/OH during the formulation.

Several important hydroxyl-containing functional groups in lignins such as phenolic and aliphatic hydroxyl groups as well as carboxylic acids are classified and their contents are determined quantitatively by employing ^{31}P NMR spectroscopy. The content and classification of these functional groups play an important role in determining their compatibilities during the process of chemical polymerization.

The technique has been successfully implemented for the absolute determination of various phenolic and non-phenolic structures in several native and technical lignins [67–72]. The availability of a phosphitylating reagent [71] that permits excellent resolution and the quantitative spectroscopic detection of several phenolic moieties with varying substitution patterns provide an excellent opportunity for systematically exploring the complex reactions that occurs in lignin during several different pulping processes. The phosphitylating reagent (2-chloro-1,3,2-dioxaphospholane) or reagent I provides essential information about primary hydroxyl groups along with both *erythro* and *threo* diastereomers of the arylglycerol- β -aryl ether structures. The phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane) or TMDP is a powerful analytical tool for distinguishing between different phenolic condensed units such as diphenylmethanes (DPM), diaryl ethers (4-O-5') and biphenolics (5-5') as well as benzylic and terminal carboxylic acids in lignin (**Figure 3**).

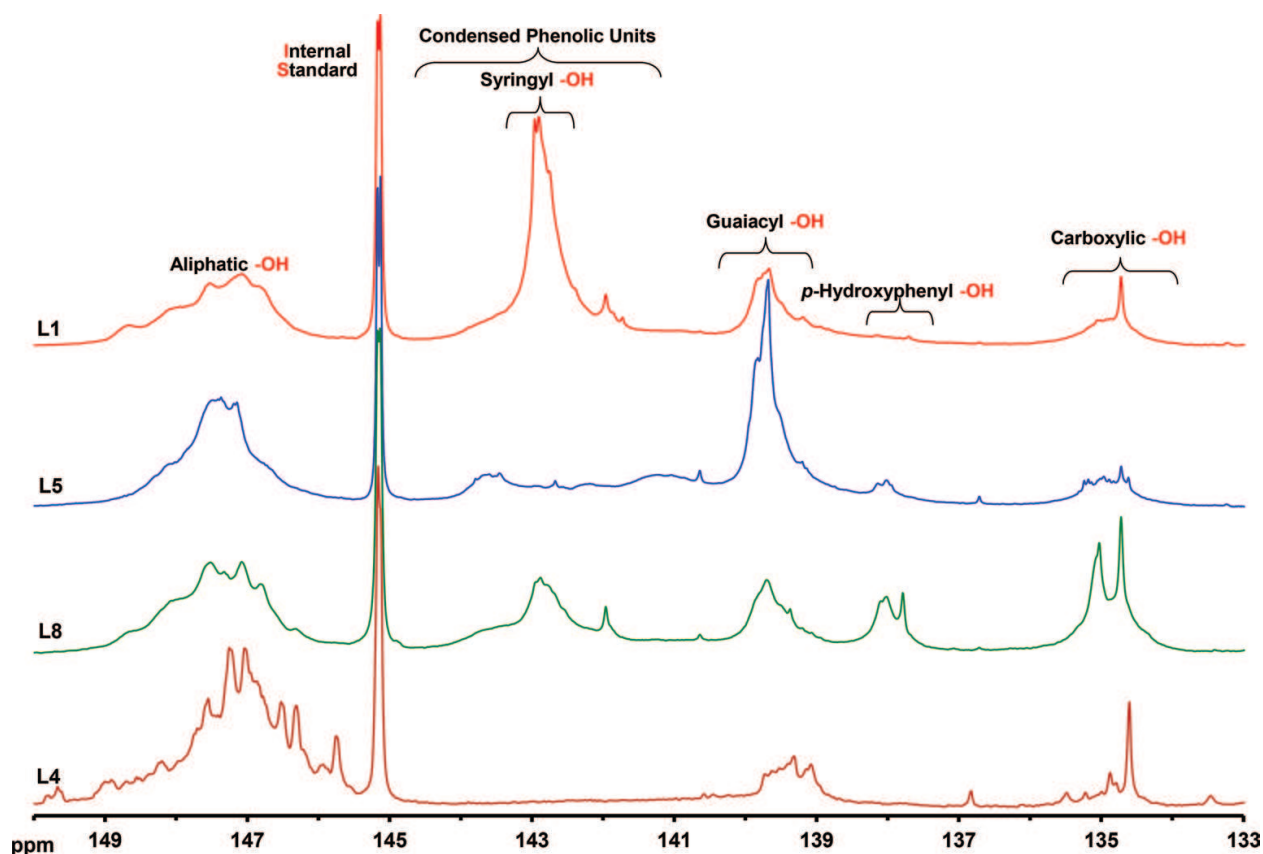


Figure 3. ^{31}P NMR spectra and signal assignments of hardwood kraft (L1), softwood Indulin AT (L5), Aldrich (L4) sodium lignosulfonates and wheat straw soda (L8) lignins phosphitylated with TMDP.

The ^{31}P NMR spectral analysis of all four lignin samples features distinct differences in terms of the nature and the content of various lignin moieties with hydroxyl groups. The presence of both syringyl (S) and guaiacyl (G) units in L1 sample clearly confirms the lignin was recovered from hardwoods. Since softwood lignins contain almost exclusively guaiacyl, the absence of syringyl signal in L5 and L4 suggest both lignin samples were extracted from softwoods. However, L5 was extracted under alkaline kraft while L4 was extracted under acid sulfite pulping processes. The ^{31}P NMR signal for aliphatic hydroxyl groups isolated from kraft lignin is often recorded as a smooth broad band. The same NMR signal for lignosulfonates is significantly different. The signal is always branched and lopsided. The L8 lignin was recovered from agro-residues. Its ^{31}P NMR spectrum exhibited high concentration of carboxylic acids, typical of soda lignin [73, 74] with a similar ratio of the benzylic to the terminal type. In addition, the lignin contains several distinct signals corresponding to all three different (G:S:H) monomeric components of lignin.

In addition to quantitative determination of several different classes of hydroxyl groups in several lignin samples, their quantities were also normalized. This is a recommended approach for determining the contribution of lignin hydroxyl units toward the reaction with other polymeric precursors in consideration of biomaterial fabrications. **Table 3** represents the percent distribution of four major lignin functional groups by quantitative ^{31}P NMR spectroscopy.

³¹ P NMR analysis mmol/g & (%)	L1	L2	L3	L4	L5	L6	L7	L8
Carboxylic –OH								
	0.34(6.1%)	0.24(4.8%)	0.51(6.8%)	0.10(4.9%)	0.35(6.1%)	0.40(10.4%)	0.75 (13.6%)	0.91(17%)
Non-condensed phenolic –OH								
G ^a	0.85(15.4%)	0.93(18.7%)	0.87(11.6%)	0.21(10.3%)	1.97(33.9%)	0.61(15.8%)	0.96 (17.5%)	0.74(13.8%)
S ^b	2.22(40.1%)	1.72(34.5%)	0.00	0.00	0.00	0.60(15.6%)	0.87 (15.8%)	0.77(14.4%)
H ^c	0.06(1.1%)	0.15(3.0%)	0.03(0.4%)	0.00	0.26(4.5%)	0.05(1.3%)	0.33 (6.0%)	0.41(7.7%)
Sum	3.13(56.6%)	2.80(56.2%)	0.90(12.0%)	0.21(10.3%)	2.23(38.4%)	1.26(32.7%)	2.16 (39.3%)	1.92(35.9%)
Condensed phenolic –OH								
DPM ^d	N/A	0.28(5.6%)	0.02(0.3%)	0.00	0.34(5.8%)	0.14(3.6%)	0.15 (2.7%)	0.23(4.3%)
4-O-5 ^e	N/A	N/A	0.15(2.0%)	0.00	0.45(7.7%)	N/A	N/A	N/A
5-5 ^f	0.36(6.5%)	0.37(7.4%)	0.12(1.6%)	0.00	0.41(7.0%)	0.49(12.7%)	0.30 (5.5%)	0.26(4.9%)
Sum	0.36(6.5%)	0.65(13.0%)	0.29(3.9%)	0.00	1.20(20.5%)	0.63(16.3%)	0.45 (8.2%)	0.49(9.2%)
Aliphatic–OH	1.70(30.7%)	1.29(25.9%)	5.83(77.4%)	1.73(84.8%)	2.04(35.1%)	1.56(40.5%)	2.14 (38.9%)	2.03(37.9%)
Total	5.53	4.98	7.53	2.04	5.82	3.85	5.50	5.35

^aGuaiacyl –OH.

^bSyringyl –OH including diphenylmethane (DPM) and/or diaryl ether (4-O-5') for L1, L2, L6, L7.

^c*p*-Hydroxyphenyl –OH.

^dDiphenylmethane.

^eDiaryl ether.

^fBiphenolic 5-5'.

Table 3. Quantitative ³¹P NMR determination of carboxylic, phenolic, condensed structures and aliphatic hydroxyl groups present in the lignins [44, 45].

The percent aliphatic hydroxyl units were found to be the highest for both the L4 and L3 sample of lignosulfonates, respectively, even though the L3 contained 4.1 mmole/g more aliphatic hydroxyl units than L4 sample. Both hardwood lignin samples (L1 and L2) contained the most non-condensed hydroxyl units due to the presence of both guaiacyl and syringyl units while the most condensed units were present in the Indulin AT. Soda lignins from the agricultural residues were found to have most carboxylic acids.

It is imperative to point out that despite the higher reactivity of phenolic hydroxyl groups, the benzylic hydroxyl groups were shown to be more reactive than phenolic hydroxyl groups toward diisocyanates [40, 41]. Studies with several lignin-like model compounds and aliphatic isocyanate, lignin polymer and aliphatic isocyanate, and lignin models and polyisocyanates have all lend a hand to similar observation [75, 76]. These experimentations indicate the most suitable lignin for partial polyols substitution should contain high benzylic hydroxyl group (α -hydroxyl and γ -carbinol) content and have little or no phenolic hydroxyl groups.

Direct lignin substitution in formulation of biofoams was achieved successfully [77]. The physical properties of the obtained PU foams are reported in **Table 4**. Since the density of the PU biofoams with lignin was comparable with the PU foam reference thus it was possible to compare their opening cell content and thermal conductivity. The opening cell content of the PU biofoams were reported to be quite similar with that of the reference indicating that lignin did not modify the cellular structure and did not cause cellular wall collapse as shown in **Figure 4**. It was interesting to observe that the thermal conductivity of the lignin-PU foams was much closed to that of the PU reference.

Direct substitution of lignin in PU biofoams formulation is not very effective. The extent of its substitution is limited by the active aliphatic hydroxyl groups, their abundance and order of their reactivity which influence lignin solubility. Other factors such as the presence of phenolic groups, carbohydrate impurities, ash content, particle size, molecular weight, rheology, dispersity and the type of lignin recovery play important role in its performance as a precursor during manufacturing of biofoams.

The application of lignosulfonate as a partial substitute for petroleum-based polyol during preparation of PU biofoam was evaluated. Three different PU biofoams were prepared with direct substitution of lignosulfonates at 10–12, 25 and 50%wt in lieu of conventional polyols. The PU biofoams corresponding to each concentration were dispersed in aqueous solution at room temperature over 10 days. The supernatant were freeze-dried and the weight of the leached lignosulfonates was determined. The weight was compared to the dried PU biofoams and a mass balance was established. The image of **Figure 5** and the data in **Table 5** clearly show that in spite of formation of PU biofoams, lignosulfonate did not completely undergo reaction as polyols with aromatic diisocyanates but rather participated as fillers. This was concluded due to low pKa of sulfonates ($\text{pKa} \leq 2$), and could only be evaluated in this fashion since lignosulfonates are water soluble lignins.

Sample	Density (kg/m ³)	Opening cell (%)	Thermal conductivity (W/m.K)
Without lignin	33.06	10.7	0.0250
10% lignin	33.42	10.8	0.0255
20% lignin	34.04	10.9	0.0252

Table 4. Physical properties of the rigid PU foams [77].

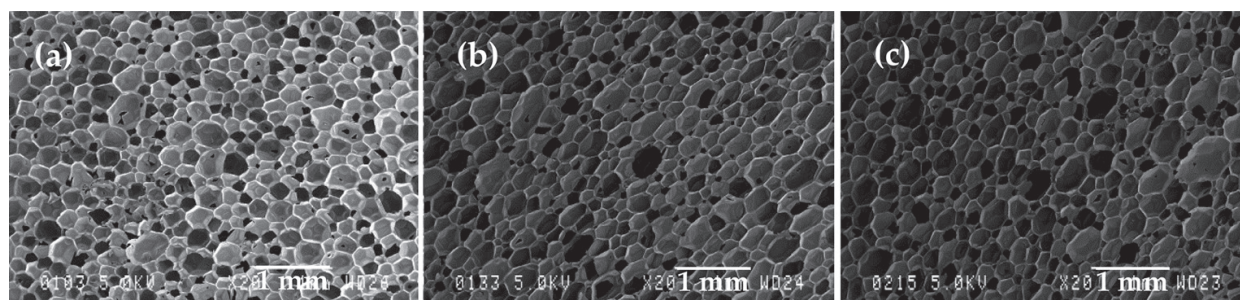


Figure 4. SEM image of PU (a) without lignin, (b) 10 wt% and (c) 20 wt% lignin [77].

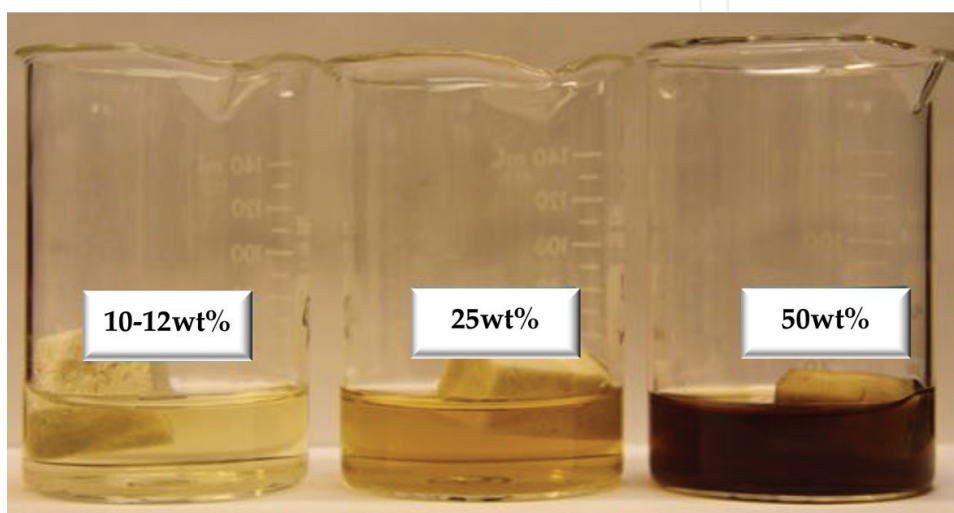


Figure 5. Images of lignosulfonates leaching out of PU biofoam in water.

Lignin concentration (wt%)	Lignin loss (w/w%) (extracted lignin)	Lignin loss (w/w%) (PU weight)	Lignin loss (w/w%) (mass balance)
10–12	2.5 ± 0.4	3.0 ± 0.2	2.5–3.0
25	8.7 ± 1.8	9.5 ± 1.5	8.7–9.5
50	23.1 ± 0.7	28.4 ± 0.5	23.1–28.4

Table 5. Determination of leached lignosulfonates in water from the rigid PU biofoams.

2.2. Lignin and polyols

Addition of lignin affects both thermal and mechanical properties of polyurethane. The extent of changes in polyurethane networks properties is suggested to be related to the preparation method and the lignin content [78, 79].

The performance of lignin and polyurethane products may be improved by the addition of other polyols [80, 81] such as polyethylene glycols (PEG), polypropylene glycols (PPG), and other chain length of the polyether polyols during the copolymerization process [82].

The addition of PEG and PPG affects the flexibility and rigidity of the polyurethanes. In particular, the molecular weight of PEG influences tensile strength of polyurethanes. Both thermal and mechanical properties of the polyurethanes can be controlled by changing the amounts of lignin and polyol [28, 83]. In this method, lignin is often dissolved in polyols before reacting with diisocyanates. The isocyanate functional group would act as cross-linking agent, connecting the lignin and polyols. To obtain greater cross-link density and better mechanical properties, greater NCO/OH ratio is required and this parameter becomes more important as the lignin concentration increases [84, 85]. The key parameter to this reaction is highly dependent on the lignin hydroxyl groups and their interactions with polyols.

The reactivity of polyol with lignin was examined by addition of polyester polyol to lignin. A sample of commercially available polyester polyol, which is currently utilized in PU production, was examined for its chemical compositions and interaction with several lignin samples. The ^{31}P NMR spectroscopy technique for quantitative determination and classification of the polyol hydroxyl content was performed. In this study, two different phosphitylating reagents were utilized to elucidate hydroxyl contribution of polyol toward diisocyanates during PU polymerization. The total $-\text{OH}$ content were quantitatively determined to be 7.47 and 7.50 mmol/g. The ^{31}P NMR spectra of polyol with TMDP reagent as illustrated in **Figure 6** shows a major signal (triplet) in the aliphatic region of ^{31}P NMR spectra corresponding to the presence of aliphatic hydroxyl groups. A closer examination of the ^{31}P NMR spectra also revealed the presence of additional aliphatic hydroxyl units in the same region as well as trace

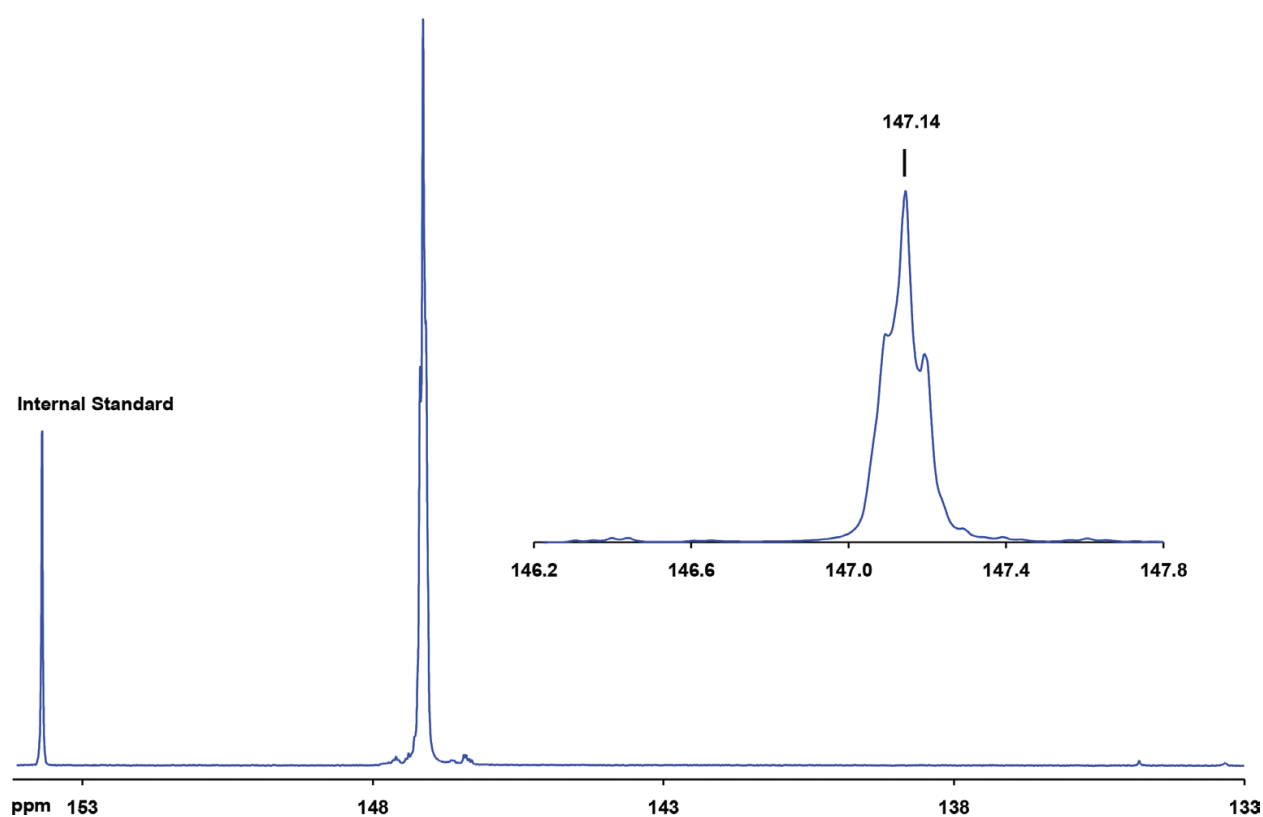


Figure 6. ^{31}P NMR spectra of polyester polyol with TMDP.

amount of carboxylic acids at 134.7 ppm. This information coupled with FTIR [86] confirmed that the commercially available polyol is a polyester-based polyol.

In a typical experiment, lignin samples were mixed and were allowed to react with the commercially available polyester polyol. The isolated products were then washed several times, purified and examined by employing ³¹P NMR spectroscopy for quantitative determination of different classes of hydroxyl groups. The ³¹P NMR spectra of these samples as shown in **Figure 6** exhibit a sharp and distinct signal in the aliphatic region. The ³¹P NMR chemical shift of this new and sharp signal in all lignin samples at about 147.1 ppm strongly suggest the formation of lignin-polyols.

It is noteworthy to mention the ³¹P NMR spectrum of the original Protobind 2400 lignin sample presented a significant feature. The spectrum exhibited presence of unusual new and sharp peak at 147.04 ppm in the aliphatic region. The nature and the shape of such a signal in that region strongly suggest that aliphatic group in the original lignin has been chemically modified by the supplier.

The quantitative determination of different classes of –OH groups by ³¹P NMR spectroscopy for all treated lignins with polyol are reported in **Table 6**. The comparison of hydroxyl contents

Lignin samples	Protobind 2400		Indulin AT		Arbo™ SO1		Protobind 3000	
	L7	PL7	L5	PL5	L3	PL3	L8	PL8
³¹ P NMR analysis	mmol/g & (%)							
COOH	0.75(13.6%)	0.52(9.6%)	0.39(6.1%)	0.23(4.2%)	0.51(6.8%)	0.09(1.9%)	0.91(16.9%)	0.70(13.3%)
Non-condensed phenolic –OH								
G ^a	0.96(17.5%)	0.64(11.8%)	2.05(32.1%)	1.26(22.8%)	0.87(11.6%)	0.54(11.7%)	0.74(13.8%)	0.57(10.8%)
S ^b	0.87(15.8%)	0.62(11.4%)	0.00	0.00	0.00	0.00	0.77(14.3%)	0.63(12.0%)
H ^c	0.33(6.0%)	0.19(3.5%)	0.20(3.1%)	0.11(2.0%)	0.03(0.4%)	0.02(0.4%)	0.41(7.6%)	0.26(4.9%)
Condensed phenolic –OH	0.45(8.2%)	0.34(6.3%)	1.32(20.7%)	0.89(16.1%)	0.28(3.7%)	0.27(5.8%)	0.50(9.3%)	0.42(8.0%)
Aliphatic –OH	2.14(38.9%)	3.13(57.5%)	2.42(37.9%)	3.04(55.0%)	5.83(77.5%)	3.71(80.1%)	2.04(38.0%)	2.69(51.0%)
Total phenolic –OH	2.61(47.5%)	1.79(32.9%)	3.57(56.0%)	2.26(14.9%)	1.18(15.7%)	0.83(17.9%)	2.42(45.1%)	1.88(35.7%)
Total –OH	5.50	5.44	6.38	5.53	7.52	4.63	5.37	5.27

^aGuaiacyl –OH.

^bSyringyl –OH.

^c*p*-Hydroxyphenyl –OH.

Table 6. Quantitative determination of several hydroxyl groups in lignin before and after treatment with polyol by ³¹P NMR spectroscopy [45].

of all the lignin samples before (L) and after reaction with the commercially available polyester polyol (PL) shows significant difference in several –OH contents in lignins. The quantities of the carboxylic acids, phenolic hydroxyl and condensed phenolic units were all found to have decreased, while the primary hydroxyl content increased considerably after blending with the polyol. This information, coupled with the quantitative determination of the different classes of hydroxyl contents (**Table 6**), suggests that either lignin hydroxyl units cross-linked with the polyol during the premixing stage or, in spite of thorough washing, trace amounts of polyol were detected in all of the lignin samples, which affected the concentration of hydroxyls in the lignin [45].

Ahvazi *et al.* investigated physical and chemical characteristics of several lignin-polyol blends by several qualitative and quantitative methods in view of bio-based polyurethane applications [45]. During this study, differently isolated biomass lignins from forestry and agricultural residues were blended with polyester polyol and one with polyethylene glycol. The isolated products were examined thoroughly to elucidate subsequent lignin and polyol interactions during the premixing stage of bio-based polyurethanes formulation. They reported that polyol was detected in lignin even after vigorous washings with several organic solvents and soxhlet extraction as shown in **Figure 7**. The experimental data coupled with two-dimensional

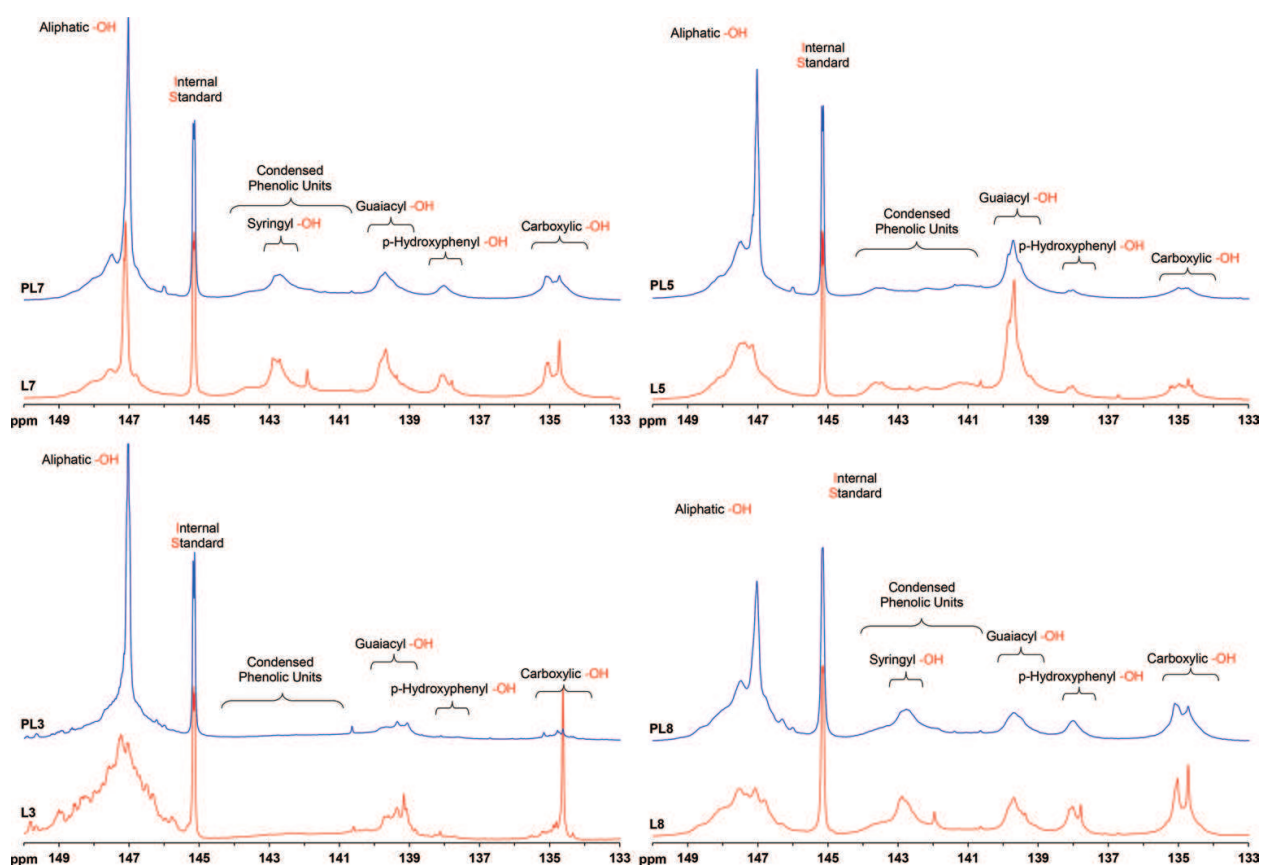


Figure 7. ^{31}P NMR spectra and signal assignments of the Protobind 2400, Indulin AT, Arbo SO1, Protobind 3000 before, (L) and after (PL) treatment with polyester polyol phosphitylated with TMDP [45].

heteronuclear multiple quantum coherence (HMQC) NMR spectroscopy confirmed the formation of lignin-polyol via strong intermolecular attractions as well as some linkages between several lignin hydroxyl and polyol functional groups.

Lignin-polyol was prepared and reported in the literature [87]. **Figure 8a** and **b** shows the optical images different solubility and compatibility of lignin in polyol. SEM images of the foams are shown in **Figure 8c** and **d** illustrating the cellular morphology at different magnifications, respectively. The cellular structure of the foam is identical in both cases, with and without lignin, which consists of regular round and closed cells. There is no significant change in the cellular size and shape as well as cellular collapse with the presence of lignin. This indicates the presence of lignin in the appropriate formulation does not alter the formation of the foam cells. In addition, there is no lignin particles could be found in the biofoams. One could speculate that lignin has been participated into the PU network structure [87].

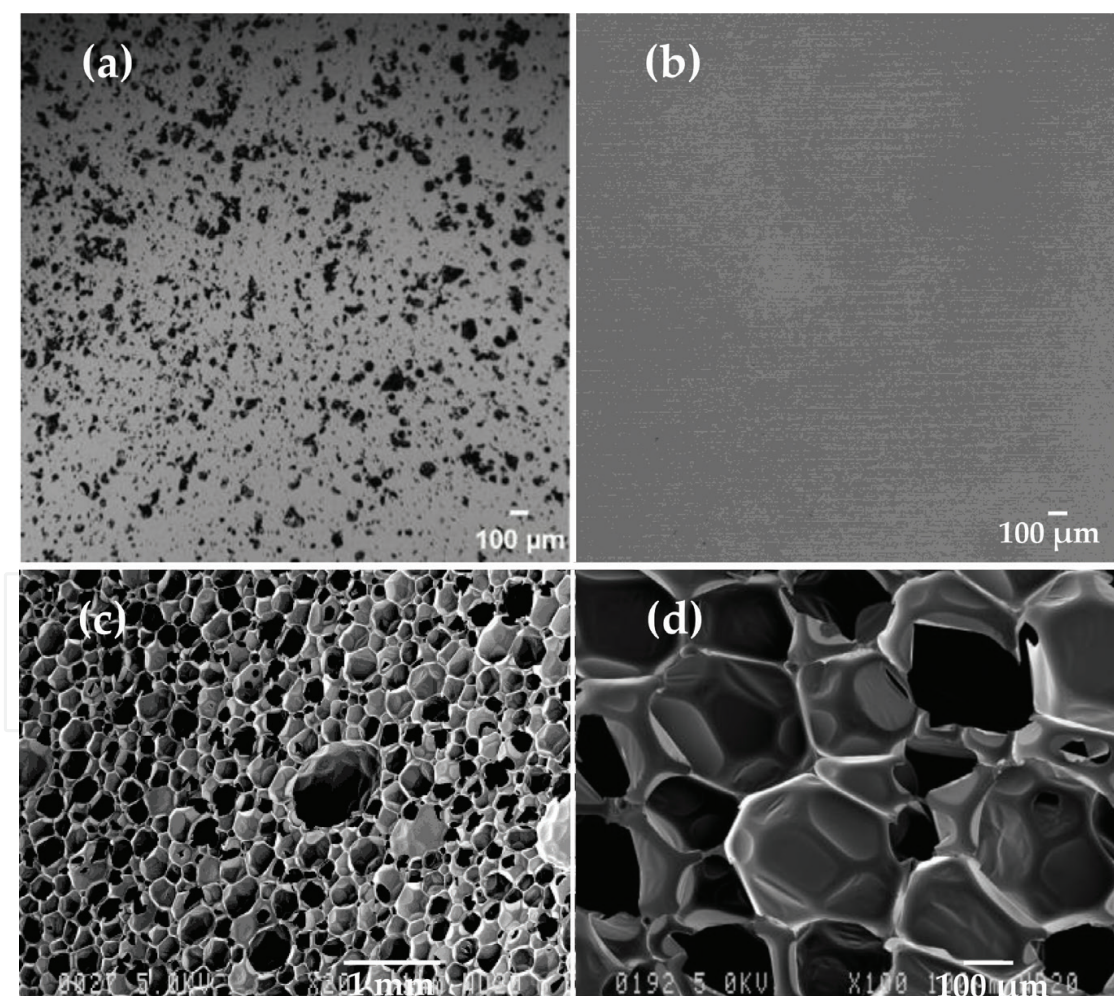


Figure 8. OM image of lingo-polyol (a) insoluble lignin, (b) soluble lignin in polyol, and SEM image for the PU foam with soluble lignin at low and high magnifications (c), (d) [87].

2.3. Chemically modified lignin

The objective of lignin modification is to increase reactivity of the lignin by modifying specific reactive groups and enhance the polycondensation process during the polyurethane production [30, 61, 62]. Chemically modified lignins provide several advantages in replacing polyols. During lignin modification, the majority of phenolic hydroxyl groups are converted to aliphatic hydroxyl units and more reactive hydroxyl groups become readily available. In addition, the steric and/or electronic constraints are also eliminated. The major drawback may be associated with its cost effectiveness. The procedure involves the conversion of phenolic hydroxyl groups to the aliphatic and more reactive hydroxyl groups. This can be achieved by either (i) direct oxyalkylation [39, 42, 88–92] or by (ii) two-steps reaction of lignin with maleic anhydride [93, 94] followed by oxyalkylation [95, 96]. The oxyalkylation are more reactive with alcohols than phenol and least with carboxylic acids in accordance to the order of nucleophilicity. During oxyalkylation, the reaction of lignin with alkene oxide would lead to chain-extended hydroxypropyl lignin and the formation of lignin-polyol derivatives [39, 42, 43]. The resulting polyols were expected to be more fluid, to possess secondary hydroxyl groups predominantly and therefore to react at lower, more convenient rates with an isocyanate-terminated prepolymer to form urethane foams with modified properties. The oxyalkylation of lignin with propylene oxide improve its solubility better than ethylene oxide.

The oxypropylated lignins were reported by Nadji et al. [62]. They noticed the oxypropylation of lignins is a straightforward process and the ensuing polyols were viscous products with functional characteristics very similar to those of conventional compounds used in the manufacture of polyurethanes that constitute the most relevant results of their investigation. They also reported that the rigid foams obtained from the polyols showed good thermal properties and dimensional stability, even after aging. These results are very encouraging, since they concern a rational valorization of an abundant renewable industrial byproduct.

Berrima et al. reported that soda lignin (L) was converted into liquid polyols by oxypropylation with propylene oxide (PO) and potassium hydroxide as a catalyst [97]. The obtained polyols were viscous liquids and possessed relatively high hydroxyl index. These two parameters were close to those of commercial polyols used in a similar context and opened the way of testing them in this field of application. The study also noticed that rigid lignin-based polyurethane foams were elaborated and displayed very promising properties as shown in **Table 7**. These materials can be used for thermal and acoustic insulation.

Ahvazi et al. reported that chemical modification of the lignin with propylene oxide to form lignin-polyol derivatives [98]. In their study, the chemical modification was performed by a two-step reaction of lignin with maleic anhydride followed by propylene oxide and by direct oxyalkylation under acidic and alkaline conditions. The physical and chemical properties of lignin-polyols from each method and the subsequent chain-extended hydroxyl groups were evaluated. They concluded that direct oxyalkylation of lignin under alkaline conditions was more efficient than acidic conditions and more effective than the two-step process for

Parameters	L	L + MA	L + MA + PO
³¹P NMR analysis	mmol/g & (%)		
COOH	0.97(17.2%)	2.87(76.5%)	0.18(6.9%)
Non-condensed phenolic –OH			
G ^a	0.79(14.0%)	0.28(7.5%)	0.13(5.0%)
S ^b	0.82(14.6%)	0.23(6.1%)	0.16(6.1%)
H ^c	0.45(8.0%)	0.16(4.3%)	0.06(2.3%)
Condensed phenolic –OH	0.48(8.5%)	0.13(3.5%)	0.18(6.9%)
Aliphatic –OH			
1°	1.61(28.6%)	0.07(1.9%)	0.72(27.6%)
2° (<i>erythro & threo</i>)	0.51(9.1%)	0.01(0.3%)	1.18(45.2%)
Total phenolic –OH	2.54(45.1%)	0.80(21.3%)	0.53(20.3%)
Total –OH	5.63	3.75	2.61
Size exclusion chromatography (GPC) (Da × 10 ³)			
Mw	229.8	237.7	309.4
Mn	136.9	90.51	260.1
Polydispersivity			
Mw/Mn	1.68	2.36	1.19
dn/dc	0.151	0.150	0.102
Differential scanning calorimetry			
ΔC _p (J/g·°C)	1.258	2.322	0.986
T _g (°C)	104.39	89.22	59.00

^aGuaiacyl –OH.

^bSyringyl –OH.

^cp-Hydroxyphenyl –OH.

Table 7. Characterization of modified wheat straw soda lignin with the two-step oxyalkylation method [98].

preparing lignin-polyol with higher aliphatic hydroxyl contents. The overall lignin modification would convert phenolic hydroxyl groups to a longer branched polyether with a hydroxyl group at the end as illustrated in **Figure 9**.

The comparison of ³¹P NMR spectra of two-step modification (L + MA + PO) to the starting material and the direct maleated lignin (L + MA) demonstrates two significant phenomena [98]. The L + MA + PO spectrum coupled with the quantitation data of **Table 7** indicates that carboxylic acids did not completely undergo transformation to their corresponding aliphatic groups during hydroxypropylation. This is expected because oxyalkylation is less reactive

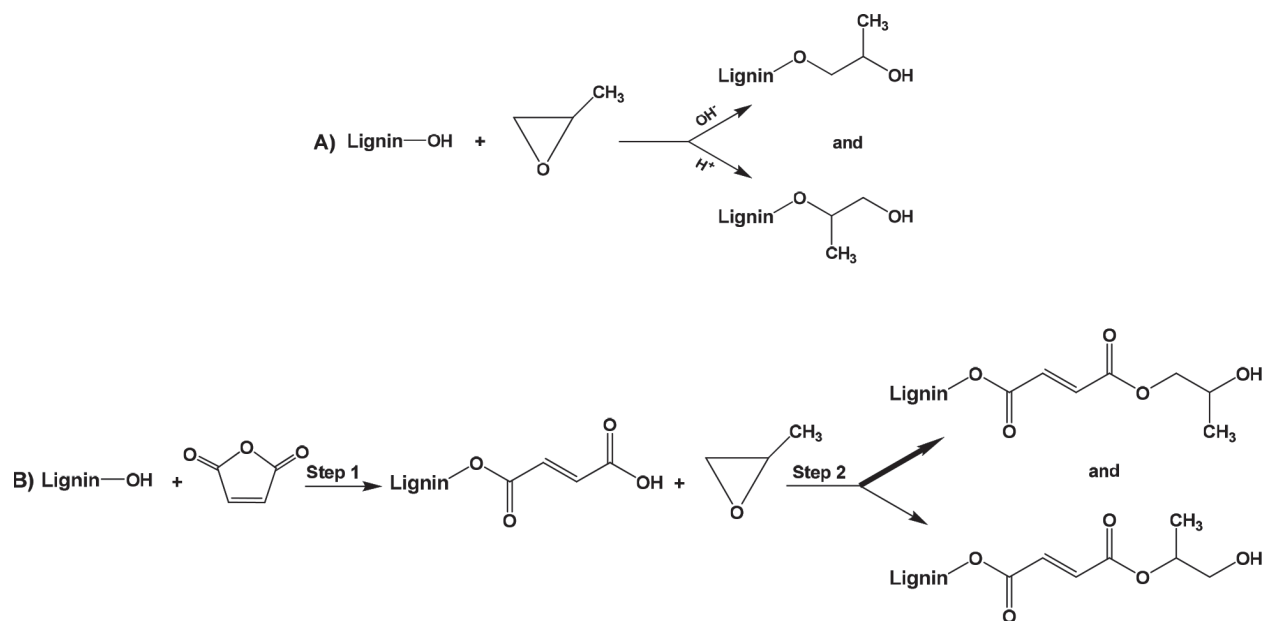


Figure 9. Schematic diagrams of direct and two-step oxyalkylation methods of hydroxyl groups in lignin [98].

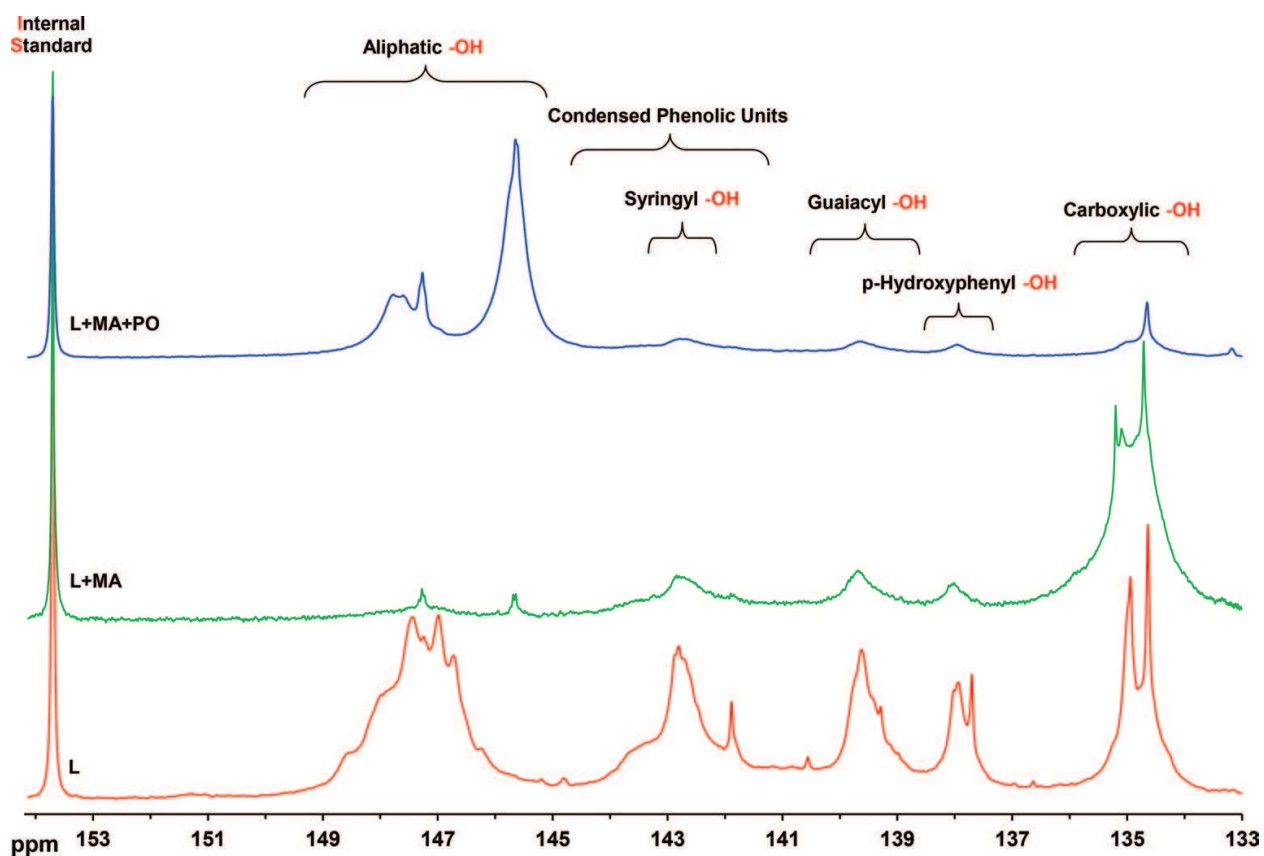


Figure 10. ³¹P NMR spectra and signal assignments of wheat straw lignin (L) derivatized with maleic anhydride (L + MA) followed by propylene oxide (L + MA + PO) with TMDP [98].

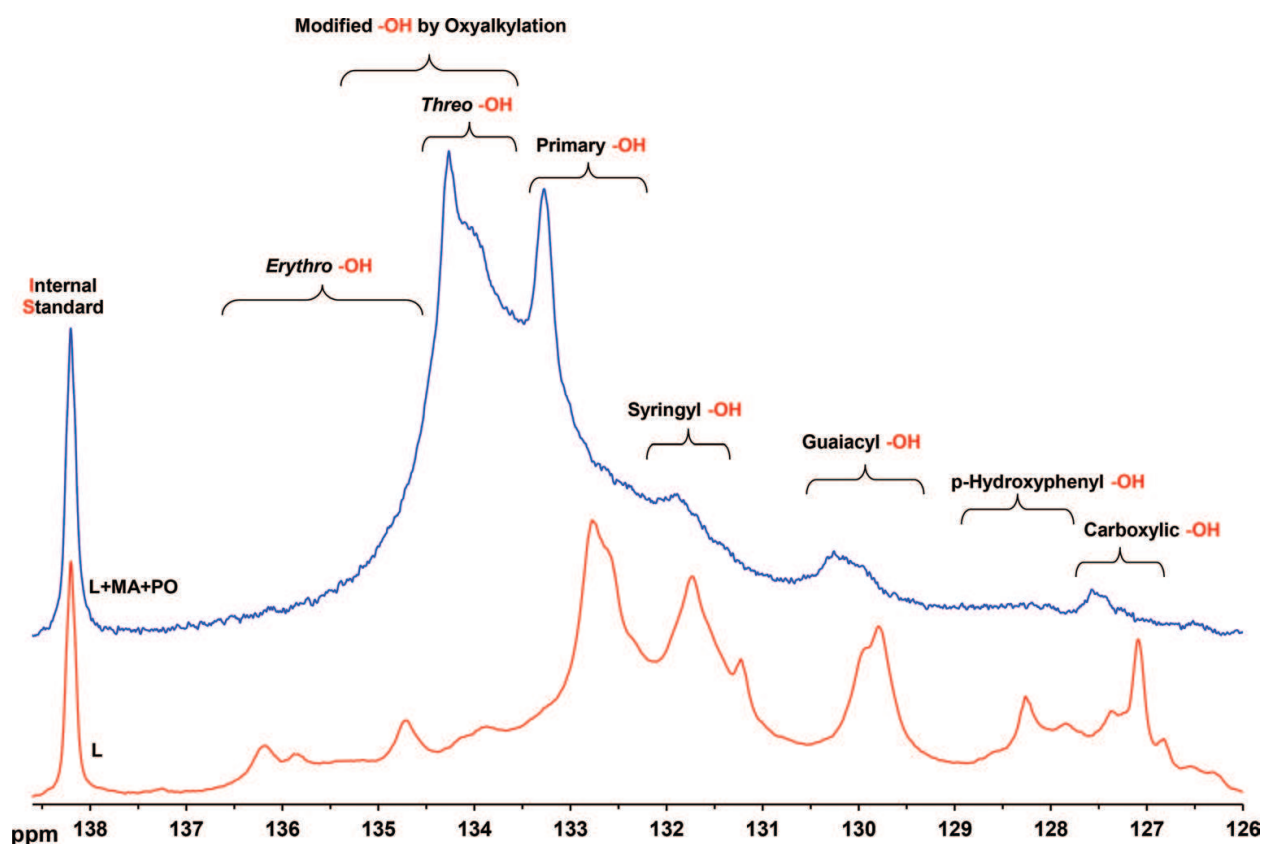


Figure 11. ^{31}P NMR spectra and signal assignments of wheat straw lignin before (L) and after modification with maleic anhydride and propylene oxide (L + MA + PO) with reagent I [98].

with carboxylic acids than the other functional groups, as 0.18 mmol/g or 6.9% of carboxylic acids remained unreacted. Indeed, the signal assignment of remaining terminal carboxylic acids recorded at 134.6 ppm in the ^{31}P NMR spectrum (**Figure 10**) shows that among the two types of carboxylic acid groups, the benzylic type was more reactive than the terminal type toward subsequent chemical modification with propylene oxide. The other phenomenon was the appearance of two different and distinct broad signals in the aliphatic region of ^{31}P NMR spectra recorded between 149.5 and 146.7 ppm and between 146.5 and 144.1 ppm. The signal recorded between 149.5 and 146.7 ppm appears in the same region as the aliphatic hydroxyl groups of the starting material. However, the signal recorded between 146.5 and 144.1 ppm was shifted upfield from the aliphatic region, and it is seemingly attributed to the hydroxypropylation reaction. To further help identify and classify these two signals, L + MA + PO was examined with reagent I and compared to the spectrum of the starting material as presented in **Figure 6**. The ^{31}P NMR spectral analysis of L + MA + PO with reagent I clearly reveal the presence of two distinct signals in the aliphatic region. The signal recorded between 133.6 and 132.1 ppm (primary $-\text{OH}$) appears in the same region as the aliphatic hydroxyl groups of the starting material. However, the other signal recorded between 136.6 and 133.6 ppm indicates the formation of new hydroxyl groups recorded in the area that is designated only to the secondary alcohols and assigned to both *erythro* and *threo* diastereomers of the arylglycerol- β -aryl ether structures ($\text{C}\alpha$ -aryl) in lignin [29] (**Figure 11**).

3. Conclusion

In this study, two ^{31}P NMR reagents were utilized effectively to quantify several different $-\text{OH}$ functional groups in different lignin samples from forestry and agriculture residues. The experimental data suggest that the application of lignin as a substitute for petroleum-based polyols in formulation of PU is limited not only by its aliphatic hydroxyl content but also with other features. Factors such as lignin extraction method, impurities, molecular weight, ash content and other features attribute to its solubility and compatibility with polyols. To obtain superior PU network film, lignin could be mixed with polyols to improve its solubility and homogeneity prior to reaction with diisocyanates. Chemical modification with two separate methods has shown that direct PO modification of lignin is more efficient and economically feasible. This method is highly to generate secondary $-\text{OH}$ groups in lignin.

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