Formation of Ligno-Polyols: Fact or Fiction

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The physical and chemical characteristics of several lignin-polyol blends were investigated by qualitative and quantitative methods from the view of biobased polyurethane applications. Four differently isolated biomass lignins from forestry and agricultural residues were blended with polyester polyol, and one was blended with polyethylene glycol. The isolated products were examined thoroughly to elucidate the subsequent lignin and polyol interactions during the premixing stage of biobased polyurethane formulation. Polyol was detected in lignin even after vigorous washings with several organic solvents and Soxhlet extraction. The experimental data coupled with two-dimensional heteronuclear multiple quantum coherence (HMQC) and nuclear magnetic resonance (NMR) spectroscopy confirmed the formation of ligno-polyols *via* strong intermolecular attractions, as well as some linkages between several lignin hydroxyl and polyol functional groups.

Keywords: Lignin; Polyester polyol; Ligno-polyol; ^{31}P NMR spectroscopy; 2D HMQC; FTIR

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INTRODUCTION

Lignin incorporation in polyurethane (PU) production has been one of the most intensively investigated lignin applications (Saraf *et al*. 1985; Yoshida *et al*. 1987; Natansohn *et al*. 1990; Evtuguin *et al*. 1998; Vanderlaan and Thring 1998; Cateto *et al*. 2008). The addition of lignin affects both the thermal and mechanical properties of PU. The extent of the changes to the PU network properties has been suggested to be related to the preparation method and lignin content (Ciobanu *et al*. 2004; Hatakeyama *et al*. 2008). Several studies have suggested that the solubility and uniformity of the lignin are the key parameters that affect its reactivity as a substitute for polyol in PU fabrication (Hsu and Glasser 1976; Saraf *et al*. 1985; Rials and Glasser 1986; Mörck *et al*. 1988; Ciobanu *et al*. 2004; Hatakeyama *et al*. 2008). Lignin substitution in PU could be achieved directly by the combination with polyol (Yoshida *et al*. 1990; Evtuguin *et al*. 1998; Vanderlaan and Thring 1998; Cateto *et al*. 2008) or through chemical modifications (Glasser 1989; Gandini *et al*. 2002; Nadji *et al*. 2005; Ahvazi *et al*. 2011).

A number of studies have suggested that the performance of lignin and PU products may be improved by the addition of other polyols, such as polyethylene glycol (PEG), polypropylene glycol (PPG) (Saraf *et al*. 1985; Mörck *et al*. 1988), and other chain lengths of polyether polyols, during the copolymerization process (Hatakeyama *et*

al. 2003). The addition of PEG and PPG affected the flexibility and rigidity of the PU. Also, the molecular weight of PEG influenced the tensile strength of PU. Both the thermal and mechanical properties of the PU could be controlled by changing the amounts of lignin and polyol (Chahar *et al*. 2004). In this method, lignin is often dissolved in polyol before being reacted with diisocyanates. It has been suggested that the isocyanate functional group would act as a cross-linking agent, connecting the lignin and polyol. To obtain greater crosslink densities and better mechanical properties, a greater NCO/OH ratio is required. This parameter becomes more important as the lignin concentration increases (Rials and Glasser 1984; Thring *et al*. 1997).

The objective of this study was to elucidate the interaction and possible linkages that may occur between lignin and polyol when they are blended prior to substitution in a PU network. Four different isolated lignins were mixed with polyester polyol, and one was mixed with PEG. The physical and chemical characteristics of the isolated products were examined by quantitative and qualitative methods, such as ^{31}P nuclear magnetic resonance (NMR) spectroscopy to monitor the content of several different classes of lignin hydroxyl groups. In addition, two-dimensional heteronuclear multiple quantum coherence (HMQC) experiments were performed to investigate the structural characteristics and ^{1}H-^{13}C correlation of the lignin before and after blending with polyester polyol. The obtained information was aimed at addressing a number of pressing issues relevant to the process optimization of the substitution of higher lignin content in PU applications through the lignin-polyol premixing method.

EXPERIMENTAL

Materials and Methods

Lignin samples and reagents

Four different lignin samples were selected for this study. Two samples of commercially available Protobind 2400 (L1) and Protobind 3000 (L4) were provided by GreenValue (Lausanne, Switzerland). The third lignin sample, Indulin AT (L2), was obtained from MeadWestvaco (North Charleston, SC, USA). The fourth sample was a sodium lignosulfonate, Arbo™ SO1 (L3), from Tembec (Témiscaming, Canada). The polyester polyol (Stepanpol PS2532) was received from Stepan Company (Burlington, Ontario, Canada). All of the chemicals and reagents utilized in this study were purchased from Sigma-Aldrich Chemicals (Oakville, Ontario, Canada). The weight-average molecular weight (M_w) of the PEG was 3350. The aliphatic contents of the Stepanpol PS2532 and PEG were determined by ^{31}P NMR spectroscopy and found to be 4.6 mmol/g and 0.68 mmol/g, respectively.

Methods

Characterization of lignin

The lignin moisture and ash contents were determined gravimetrically according to ASTM D2974-87 (1993). The elemental analyses of the lignin samples were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Reaction of lignin with polyol

The polyol was added to the lignin at a ratio of 2:1 w/w. During each experiment, 600 mg of polyol was dissolved in 5 mL of acetone and transferred into 300 mg of lignin

dissolved in 10 mL of acetone and water (5:1, v/v), except for the lignosulfonate (1:1, v/v). The reaction was kept at room temperature for a period of 3 d under constant stirring. The reaction was stopped, and the solvent was evaporated under reduced pressure. The lignin mixture was washed three times with 40 mL of ethyl acetate and then centrifuged. The isolated materials were then washed three times with 40 mL of diethyl ether, and the lignin was isolated by filtration. The products were dissolved in a mixture of dioxane/water (1:4, v/v) and freeze dried under reduced pressure. The Soxhlet extraction was performed at 90 °C using ethyl acetate as a solvent to remove the excess polyol over nine cycles.

^{31}P nuclear magnetic resonance (NMR) spectroscopy

The quantitative ^{31}P NMR spectra of all of the lignin preparations were obtained using published procedures (Argyropoulos 1994; Granata and Argyropoulos 1995). Approximately 30 to 40 mg of dry lignin was dissolved in 500 µL of anhydrous pyridine and deuterated chloroform (1.6:1, v/v) under constant stirring. This was followed by the addition of 100 µL of cyclohexanol (23.76 mg/mL in pyridine and deuterated chloroform 1.6:1, v/v), used as an internal standard, and 50 µL of chromium(III) acetylacetonate solution (5.5 mg/mL in anhydrous pyridine and deuterated chloroform 1.6:1, v/v), used as a relaxation reagent. Finally, 100 µL of phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, TMDP) was added, and the vial was sealed and shaken to ensure thorough mixing. The mixture was transferred into a 5-mm NMR tube for subsequent NMR analyses. In the case of the lignosulfonate, the sample was dissolved in 300 µL of dimethylformamide (DMF), followed by the addition of 200 µL of anhydrous pyridine, 100 µL of cyclohexanol (23.76 mg/mL in pyridine and deuterated chloroform 1.6:1, v/v), and 50 µL of chromium(III) acetylacetonate solution (5.5 mg/mL in anhydrous pyridine and deuterated chloroform 1.6:1, v/v). Then, 100 µL of phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, TMDP) was added, followed by 125 µL of deuterated chloroform.

The NMR analyses were performed using a Bruker Avance 500 NMR spectrometer (Billerica, USA) at 298 K. The unit operated at a ^{1}H frequency of 500.13 MHz and was equipped with a 5-mm broadband inverse probe. All the ^{31}P NMR spectra were recorded with 32768 data points and a spectral width of 60606.06 Hz. The number of scans during each measurement was 512 with a relaxation delay of 5 s. The ^{31}P NMR chemical shifts were referenced at 132.2 ppm corresponding to the water signal. Bruker Topspin 2.1 software was utilized to process and analyze the data. All of the chemical shifts were reported relative to the product of TMDP with cyclohexanol as an internal standard, which was observed to have a sharp signal at 145.15 ppm for the phosphitylating reagent. The content of the hydroxyl groups was obtained by integration of the following spectral regions: carboxylic acids (135.9 ppm to 134.0 ppm), *p*-hydroxyphenyl phenolics (138.3 ppm to 137.3 ppm and 136.8 ppm to 136.5 ppm), guaiacyl phenolic hydroxyls (140.3 ppm to 138.3 ppm), syringyl phenolic units (143.1 ppm to 141.7 ppm), condensed phenolic units (DPM: 144.4 ppm to 143.1; 4-O-5': 143.1 ppm to 141.7; 5-5': 141.7 ppm to 140.8 ppm), and aliphatic hydroxyls (150.4 ppm to 145.5 ppm).

Heteronuclear multiple quantum coherence (HMQC) spectra

The NMR analyses were carried out on a Bruker Avance 500 NMR spectrometer at 298 K using DMSO-d_6 as the solvent. The HMQC spectra with sensitivity

enhancement (Cavanagh and Rance 1990; Palmer *et al*. 1991; Kay *et al*. 1992) were acquired with 160 transients per increment. The ^{1}H and ^{13}C carrier frequencies were set to 4.7 ppm and 72 ppm, respectively. All of the HMQC spectra were recorded with spectral widths of 16.02164 ppm (^{1}H) and 160 ppm (^{13}C), and with 2048 and 256 sampling points along the ^{1}H and ^{13}C dimensions, respectively. Cosine squared window functions were used along both of the time dimensions. Prior to Fourier transform (FT), linear prediction was performed at 512 points for the ^{13}C dimension. The final spectral data matrices had 2024×1024 points. After FT, the baseline of the ^{1}H dimension was corrected by a polynomial function.

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra were obtained for the powdered solid lignin on KBr discs using a Bruker Tensor Series FTIR Spectrometer (Milton, Canada) in the transmittance (TR) analysis mode. The spectra were collected from 4000 cm^{-1} to 400 cm^{-1} with 64 scans at a 2 cm^{-1} resolution.

Size exclusion chromatography

A multi-detection gel permeation chromatography from Agilent Technologies (Model 1200, Waldbronn, Germany) was utilized to perform all the analysis. This high-performance liquid chromatography system was equipped with an autosampler, column heating module, UV diode-array detector, solvent tray, degasser, quaternary pump, and LC 3D software. In addition, a Wyatt (Santa-Barbara, CA) Dawn Heleos II multi angle laser light scattering (MALLS) detector equipped with fluorescence filters on the even number detectors, and a Wyatt Optilab rEX refractive index detector were utilized. The data collection and calibration were operated with Astra 5.3.4 software from Wyatt. The separation was executed with dry BHT-stabilized THF by injecting 75 µL of acetobrominated lignin solutions into THF. Before injection into the thermostatically (25 °C) controlled columns (300 mm × 7.8 mm) of Styragel HR4, HR4E, and HR1 (Waters, Milford, MA), the sample was diluted to a 1.0 mg/mL concentration and filtered through a 0.2-µm membrane. The flow rate was 1.0 mL/min. The MALLS even number detector signals using the specific refractive index increments (d*n*/d*c*) of each sample from the refractive index detector utilized for the sample molar masses determination. The polystyrene standards from Polymer Laboratories (Amherst, MA) and Sigma-Aldrich using the molar masses determined by the manufacturers utilized for calibration curve, and the elution time from the Agilent UV detector signal at 254 nm was used for the determination of the molar masses.

The size exclusion chromatography analysis for the lignosulfonate sample was performed in an aqueous medium with 0.1 M $NaNO_3$ as an electrolyte and in a Waters 1525 pump system with 717 plus autoinjector, a flow rate of 1.0 mL/min, column heater maintained at 35 °C containing a Polysep-3000 column (30 cm, 8 m, Phenomenex, Torrance, USA), Polysep-5000 column (30 cm, 8 m, Phenomenex), Ultrahydrogel 500 column (30 cm, 10 µm, Waters), and a refractive index detector maintained at 35 °C. The data acquisition and processing were operated using Breeze software v 3.20 included by the manufacturer. The measurements were made only once. The error associated with the method was approximately 5%. The retention time for each chromatogram was corrected with ethylene glycol (EG) as an internal standard, which was used in all of the samples and standards. The number of theoretical plates, determined with an injection of EG, was 15,000 for the system. Prior to each run, the lignosulfonate sample was diluted to a

concentration of 10 mg/mL and then filtered through a 0.45-µm nylon membrane. A calibration curve using pullulan, a polysaccharide, as the standard was utilized to determine Mw.

Glass transition temperature (T_g) and differential scanning calorimetry (DSC)

The glass transition temperature (T_g) of the lignin samples was determined using a PerkinElmer Pyris 1 differential scanning calorimetry (DSC) instrument (Woodland, CA) under a nitrogen atmosphere. Prior to the T_g trials, the lignin samples were dried overnight under vacuum at 60 to 70 °C. During each trial, approximately 10 mg of dry lignin was used in an aluminum pan. The temperature program used for this study was as follows: the samples were cooled from room temperature to -40 °C at a cooling rate of 20 °C/min, held at this temperature for 1 min, then heated to 200 °C at a heating rate of 20 °C/min (first measurement cycle), held at this temperature for 1 min, cooled to -40 °C at a cooling rate of 20 °C/min, held at this temperature for 1 min, and then reheated to 200 °C at a heating rate of 20 °C/min (second measurement cycle). The T_g analysis was duplicated for each lignin sample and reported as the average. The T_g is defined as one-half of the change in the heat capacity occurring over the transition of the second heating run (Ämmälahti *et al*. 1998; Capanema *et al*. 2004).

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) images were obtained using a JEOL scanning electron microscope (JSM-6100, Tokyo, Japan) operating at a voltage of 15 kV. Prior to the SEM analysis, a 10 to 20 nm thin layer of Pd/Au was deposited on the sample using a Ted Pella 208 Sputter Coater (Redding, CA) to minimize the charge effect from the insulating properties of the samples.

RESULTS AND DISCUSSION

The physical and chemical interactions of the lignin and polyol during the premixing stage of preparing the biobased PU were investigated utilizing different types of lignin, namely Protobind 2400 (L1), Indulin AT (L2), Arbo™ SO1 (L3), and Protobind 3000 (L4). The lignin samples were characterized to determine their moisture content, ash content, molecular weight distribution (M_w/M_n), T_g, and elemental compositions, all of which are reported in Table 1.

The moisture and ash contents were determined gravimetrically. L1 and L2 were found to have the lowest (2.5%) and highest (10.5%) moisture contents, respectively. The ash content was determined to be in the same relative magnitude for L1, L2, and L4, which all had ash contents of less than 3%, while L3 was found to contain a 24% ash content. This was to be expected because lignosulfonates often contain remarkable amounts of inorganic contaminants, which may be attributed to the high concentration of elemental sulfur.

Indeed, the elemental analyses showed that L3 had the highest sulfur and oxygen contents among all of the samples because of the presence of sulfonate groups. However, L3 was found to contain the lowest carbon, hydrogen, and methoxy contents. In contrast, the carbon, hydrogen, and methoxy contents were found to be the most abundant in the L1 sample.

Table 1. Chemical and Physical Characterizations of Biomass Lignins from Forestry and Agricultural Residues

Parameters	Protobind 2400 (L1)	Indulin AT (L2)	Arbo™ SO1 (L3)	Protobind 3000 (L4)
Moisture and Ash Content (%)				
Moisture	2.48 ± 0.07	10.52 ± 0.02	4.66 ± 0.03	6.45 ± 0.02
Ash	1.12 ± 0.01	2.86 ± 0.02	24.15 ± 0.26	2.12 ± 0.03
Size Exclusion Chromatography (Da × 10^3)				
Mw	230.10	7.69	2.80	253.80
Mn	151.5	3.56	0.62	172.50
dn/dc	0.186	0.208	N/A	0.180
Mw/Mn	1.52	2.16	4.52	1.47
Differential Scanning Calorimetry				
Tg (°C)	82, 94, 137	139	121	78, 126
Elemental Analysis (%)				
C	61.55	58.86	40.99	59.75
H	6.32	6.24	4.65	6.16
N	0.79	0.59	1.09	3.10
O	29.44	30.82	37.26	28.60
S	1.19	1.32	6.63	< 0.50
OCH_3	17.21	11.72	6.74	11.20
C_9 Structural Unit	$C_9H_{9.07}O_{2.53}N_{0.11}S_{0.07}(OCH_3)_{1.092}$	$C_9H_{10.06}O_{3.08}N_{0.08}S_{0.08}(OCH_3)_{0.751}$	$C_9H_{11.16}O_{5.95}N_{0.22}S_{0.58}(OCH_3)_{0.612}$	$C_9H_{9.81}O_{2.78}N_{0.43}(OCH_3)_{0.704}$
Molecular Weight (g/mol)	195.54	194.67	255.23	190.41

The highest and lowest molecular weights per the C9 empirical unit were found for the L3 and L4 samples, respectively. This was attributed to the sulfur and oxygen contents, which were determined to be the highest for the L3 sample and the lowest for the L4 lignin sample.

The M_w and M_n distributions were determined by MALLS, and it was found that both of the lignins from the agro-residues (L1 and L4) had higher M_w and M_n values, with polydispersity values closer to unity than the other lignin samples. The Size Exclusion Chromatography analysis of the starting materials will be compared to their corresponding lignin-polyol blends and discussed later in this paper.

The selection of these lignin samples was based on their chemical composition, structural features, and isolation processes. The two industrially available lignins, Protobind 2400 (L1) and Protobind 3000 (L4), had been extracted from wheat straw by the soda process. The third lignin sample, Indulin AT (L2), was isolated by the kraft process from softwood pines, and the fourth sample was a sodium lignosulfonate (L3) extracted from softwoods by the sulfite process. The uniqueness of the chemical functionality of these diverse lignin samples made them ideal candidates as reactive monomers for monitoring and evaluating their interactions with polyols during the premixing stage of preparing the biobased PU.

In this investigation, the lignin samples were all treated with polyester polyol at 1:2 w/w ratios under similar blending conditions. The products were washed thoroughly to remove the excess polyol. The isolated materials were then subjected to ^{31}P NMR spectroscopic analysis for the quantitative determination of several different hydroxyl groups. Figures 1 to 4 represent the ^{31}P NMR spectra of these samples before (L1 to L4) and after blending (PL1 to PL4).

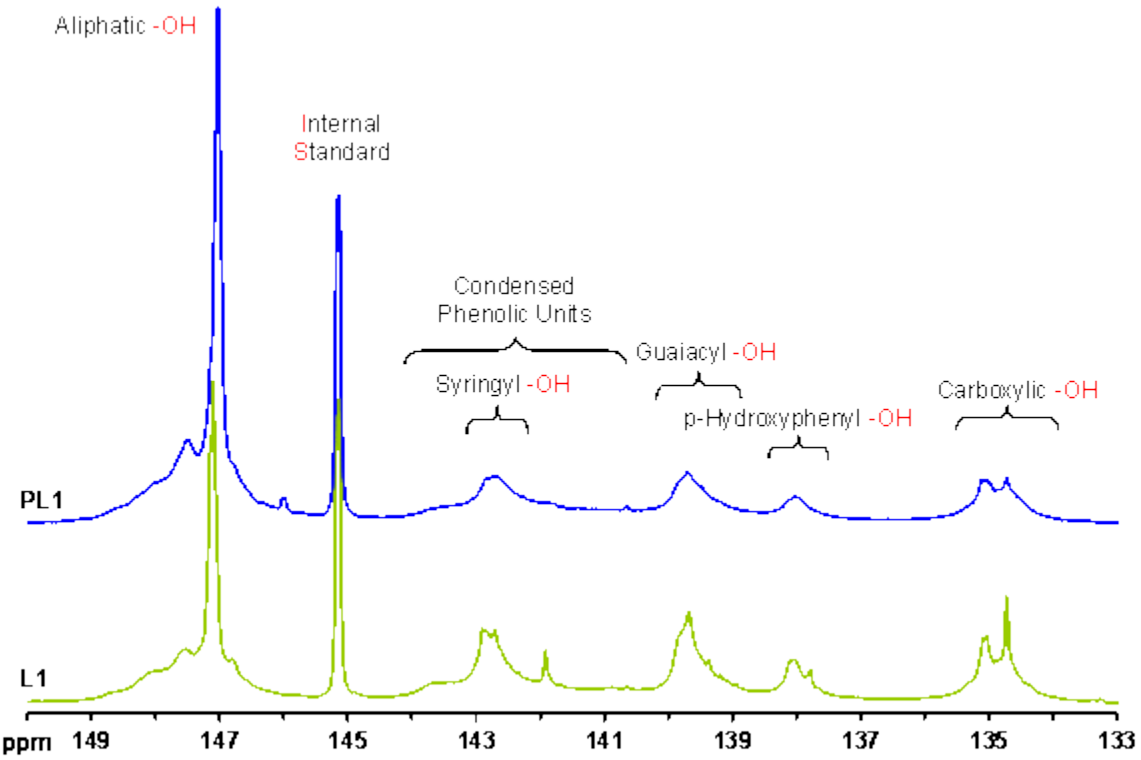


Fig. 1. ^{31}P NMR spectra and signal assignments of the Protobind 2400 before (L1) and after (PL1) treatment with polyester polyol phosphitylated with TMDP reagent

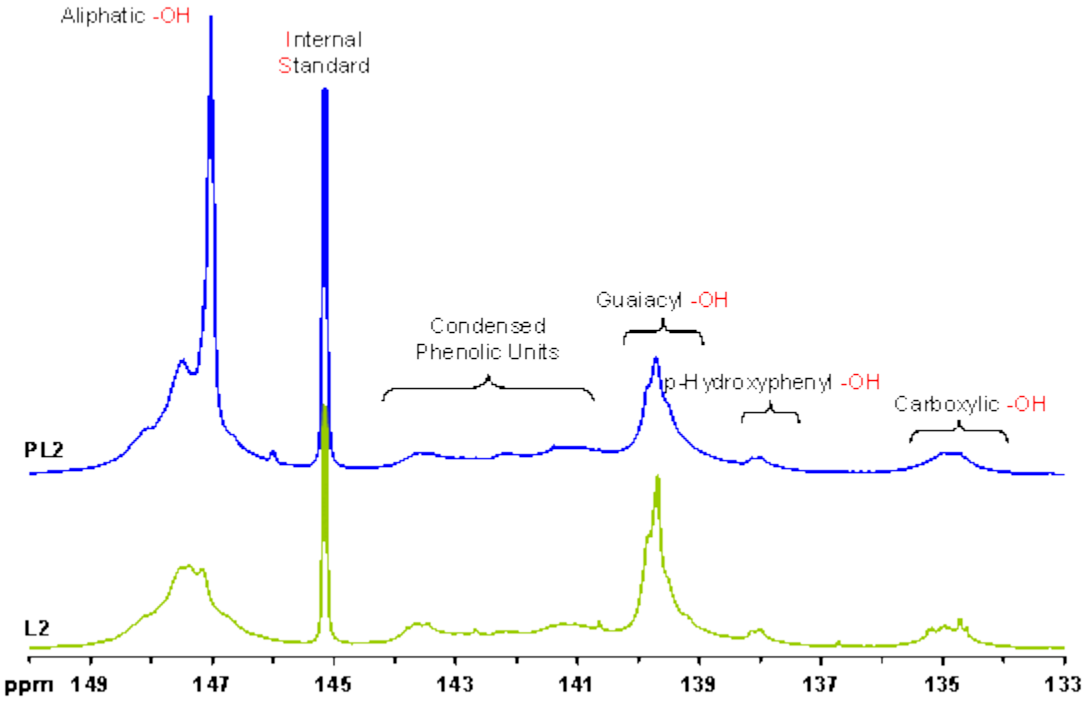


Fig. 2. ^{31}P NMR spectra and signal assignments of the Indulin AT before (L2) and after (PL2) treatment with polyester polyol phosphitylated with TMDP

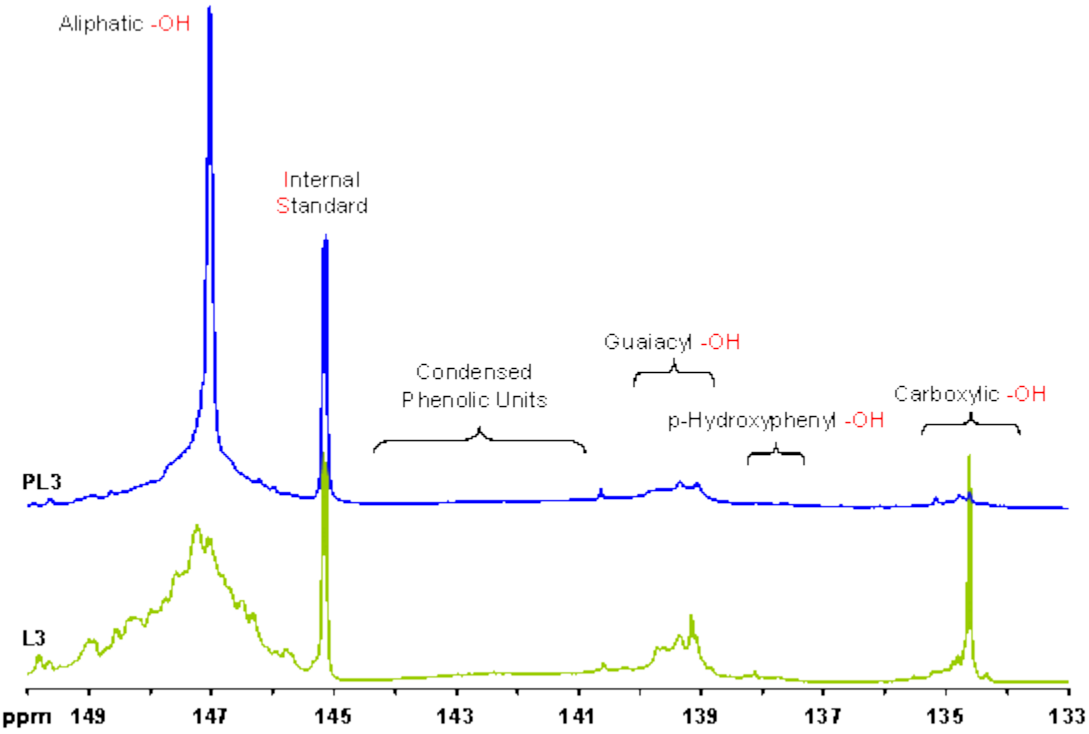


Fig. 3. ^{31}P NMR spectra and signal assignments of the Arbo™ SO1 before (L3) and after (PL3) treatment with polyester polyol phosphitylated with TMDP

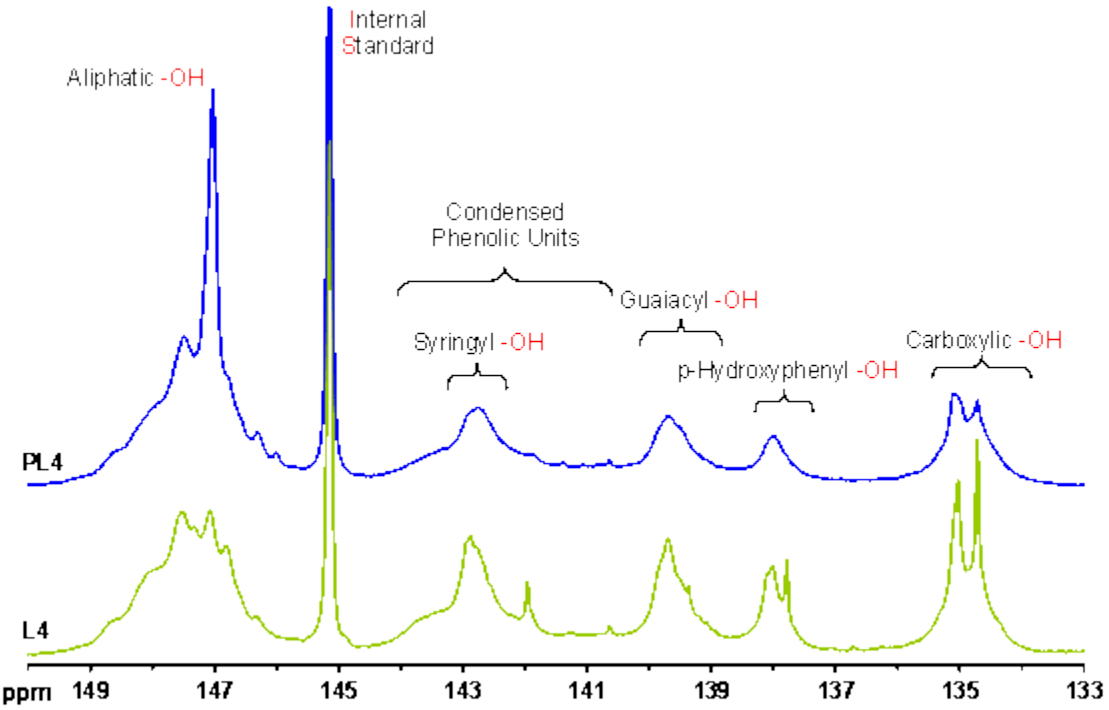


Fig. 4. ^{31}P NMR spectra and signal assignments of the Protobind 3000 before (L4) and after (PL4) treatment with polyester polyol phosphitylated with TMDP

The examination of the ^{31}P NMR spectrum for the Protobind 2400 (Fig. 1) revealed two notable features. The presence of several signals within all three major *p*-hydroxyphenyl, guaiacyl, and syringyl monomeric units were detected in the lignin from the agro-residues. These signals may have been due to the presence of some impurities during lignin recovery. The second feature was a sharp signal recorded in the aliphatic region of the ^{31}P NMR spectrum at 147.1 ppm. The presence of such a signal, which generally is not detected in a typical lignin, was attributed to the modification of the aliphatic hydroxyl groups in the lignin by the supplier.

Much like Protobind 2400, the ^{31}P NMR spectra of all four lignin samples after treatment with polyester polyol exhibited a sharp and distinct signal at 147.0 ppm in the aliphatic region. The presence of this signal was unequivocally assigned to the aliphatic hydroxyl units of the polyol, which were tightly associated with lignin after mixing. This was based on the ^{31}P NMR chemical shift of polyol recorded at 147.1 ppm. Close examination of the lignin ^{31}P NMR spectra before and after the treatment also revealed noticeable changes for several other signals. 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 2), 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.

Table 2. Quantitative Determination by ^{31}P NMR Spectroscopy of Several Hydroxyl Groups in Lignin Before and After Treatment with Polyol

Lignin Samples	Protobind 2400		Indulin AT		Arbo™ SO1		Protobind 3000	
	L1	PL1	L2	PL2	L3	PL3	L4	PL4
^{31}P NMR Analysis	(mmol/g)							
COOH	0.75	0.52	0.39	0.23	0.51	0.09	0.91	0.70
Non-condensed phenolic -OH								
G[a]	0.96	0.64	2.05	1.26	0.87	0.54	0.74	0.57
S[b]	0.87	0.62	0.00	0.00	0.00	0.00	0.77	0.63
H[c]	0.33	0.19	0.20	0.11	0.03	0.02	0.41	0.26
Condensed phenolic –OH	0.45	0.34	1.32	0.89	0.28	0.27	0.50	0.42
Aliphatic –OH	2.14	3.13	2.42	3.04	5.83	3.71	2.04	2.69
Total phenolic –OH	2.61	1.79	3.57	2.26	1.18	0.83	2.42	1.88
Total -OH	5.50	5.44	6.38	5.53	7.52	4.63	5.37	5.27

a: guaiacyl -OH; b: syringyl -OH; c: p-hydroxyphenyl -OH

To support the ^{31}P NMR spectroscopic analysis, FTIR spectroscopy was utilized to monitor and obtain more in-depth information about the possible linkages between the lignin and polyol. The FTIR spectra of all four lignins before (L1 to L4) and after blending (PL1 to PL4), as well as the polyol, are presented in Figs. 5 to 8.

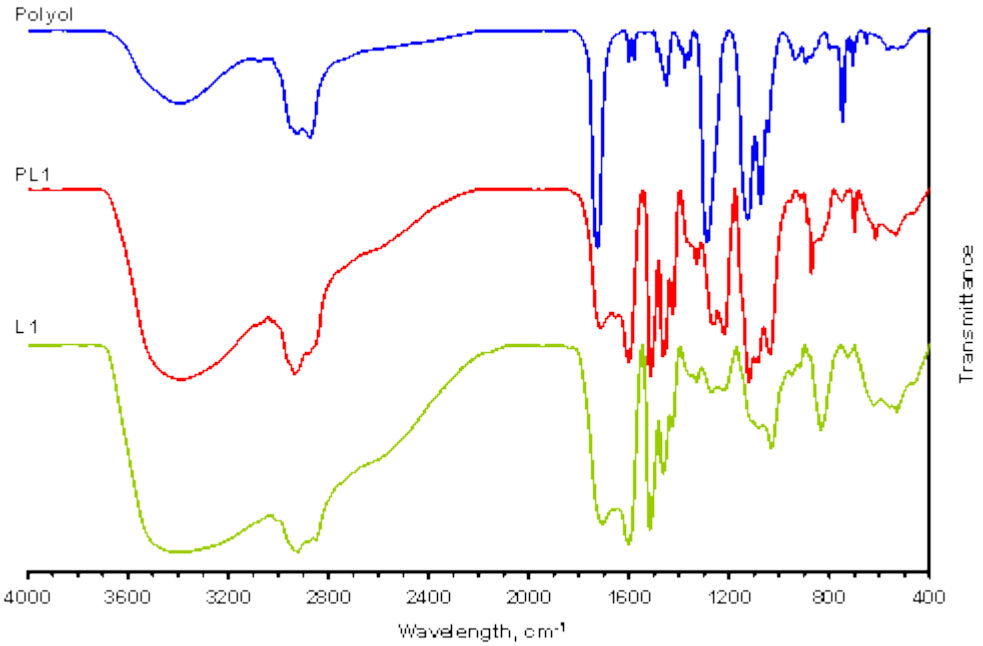


Fig. 5. FTIR spectra of the polyol and Protobind 2400 before (L1) and after (PL1) treatment with polyester polyol

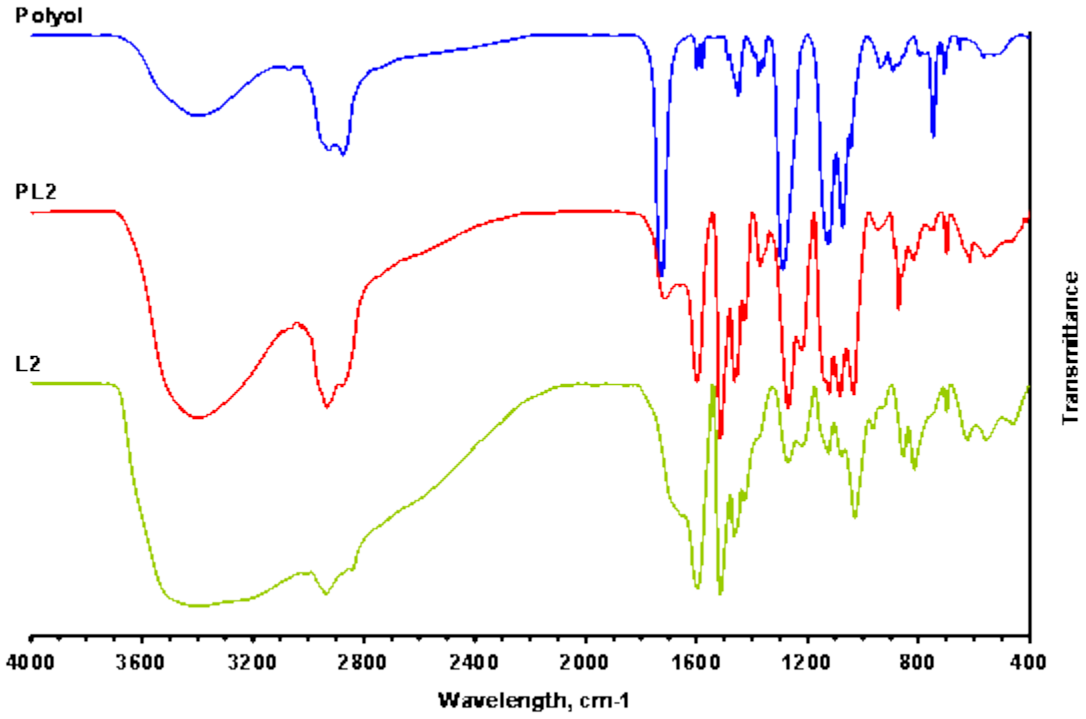


Fig. 6. FTIR spectra of the polyol and Indulin AT before (L2) and after (PL2) treatment with polyester polyol

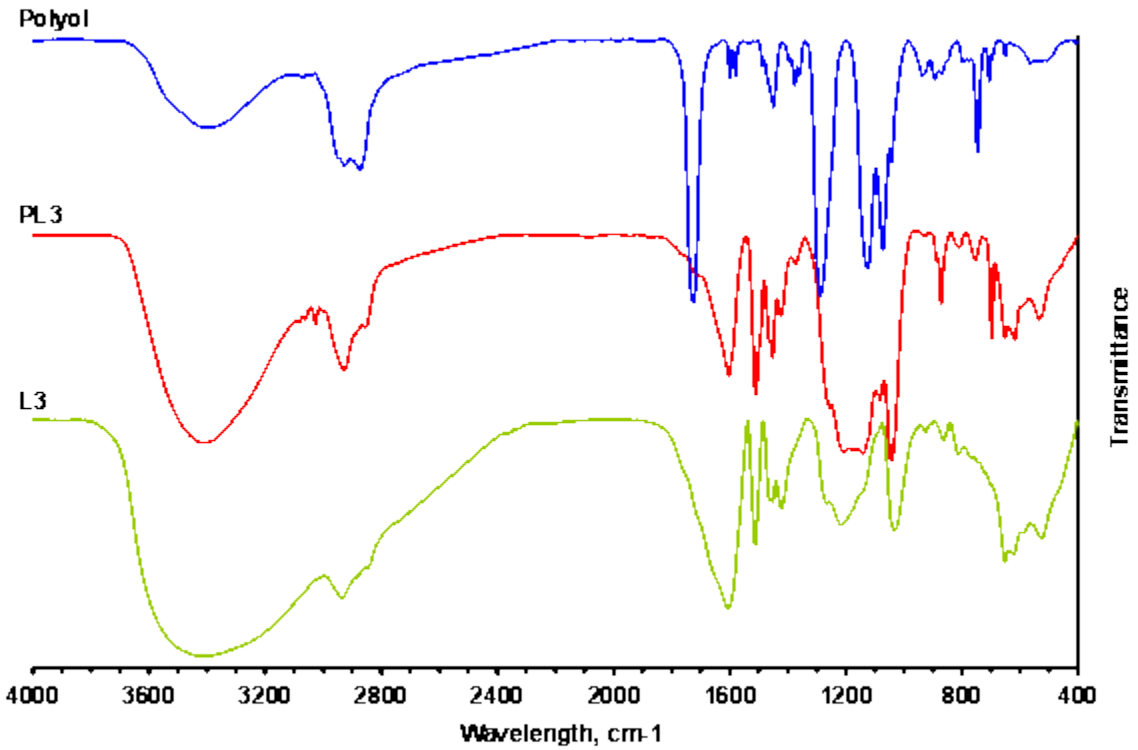


Fig. 7. FTIR spectra of the polyol and Arbo™ SO1 before (L3) and after (PL3) treatment with polyester polyol

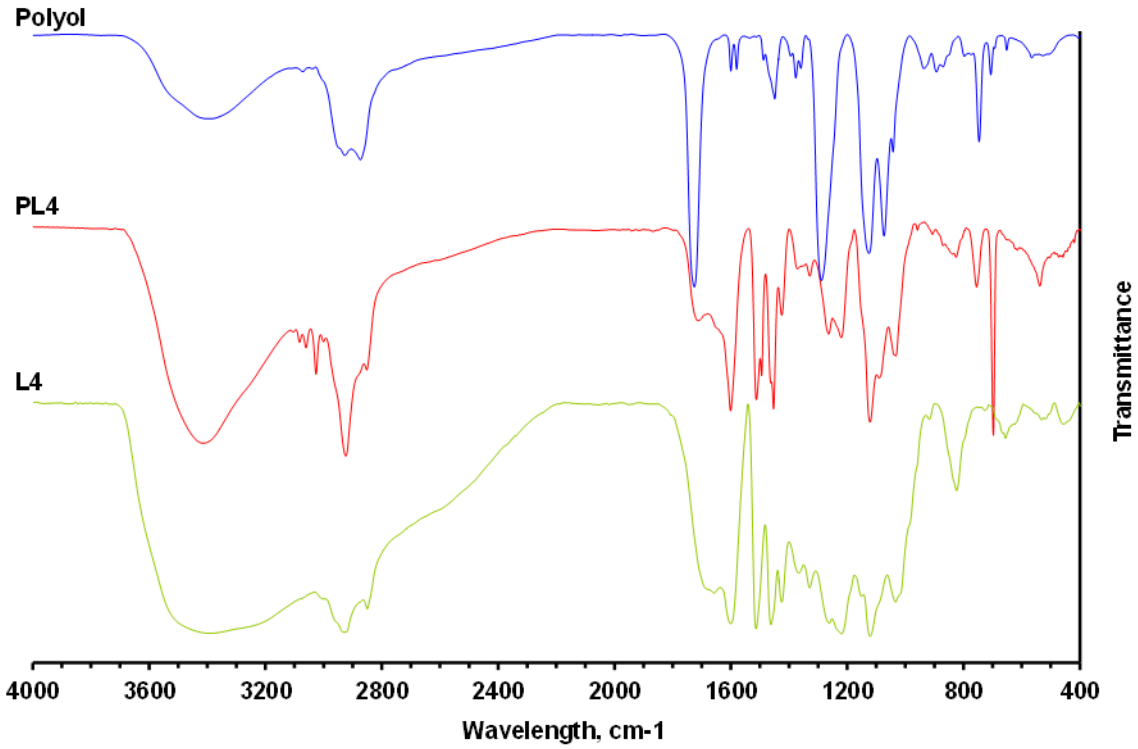


Fig. 8. FTIR spectra of the polyol and Protobind 3000 before (L4) and after (PL4) treatment with polyester polyol

Comparison of the FTIR spectra of the starting materials (L) and the polyol blends (PL) showed major alterations for several absorption bands. Some IR bands emerged after the blending process, such as the new C-H stretching bands assigned to methylene and methyl groups recorded at 2987 to 3077 cm^{-1}, carbonyl groups at approximately 1710 cm^{-1}, as well as the etherified phenols (Ph-O-C) at 698 cm^{-1}. This was found to be a common phenomenon for all of the PL samples. However, some other IR bands remained more specific in accordance with the nature of the lignins and mechanism of their formation. For example, there was a broad absorption band recorded at 2397 to 2670 cm^{-1} that was assigned to the high concentration of carboxylic acids formed during the soda pulping process of wheat straw for both the Protobind 2400 and Protobind 3000 lignin samples. A closer examination of the FTIR spectra of all four PL samples showed the formation of several new stretching vibration bands with ranges similar to carboxylic acid derivatives in the typical infrared absorption frequencies. These signals appeared at 1210 to 1320 cm^{-1} and at 1040 to 1100 cm^{-1} and corresponded to the O-C bonding of acids and alcohols, respectively. The reduction of hydroxyl contents in the PL samples coupled with the FTIR data suggested the possibility of ligno-polyol formation *via* linkages between the different classes of lignin hydroxyl units and the carbonyl group of the polyester polyol. According to Fig. 9, esters may have undergone nucleophilic substitution that is typical of carboxylic acid derivatives. Substitution occurred at the electron-deficient carbonyl carbon, and resulted in the replacement of the –OR' group with lignin hydroxyl units.

To further elucidate the role of lignin hydroxyl groups and investigate their interactions with polyols other than polyesters, Indulin AT (L2) was treated with PEG under similar conditions. The isolated product was thoroughly washed and then examined with ^{31}P NMR spectroscopy to evaluate and monitor the content of several classes of hydroxyl groups quantitatively, particularly, the aliphatic hydroxyl groups.

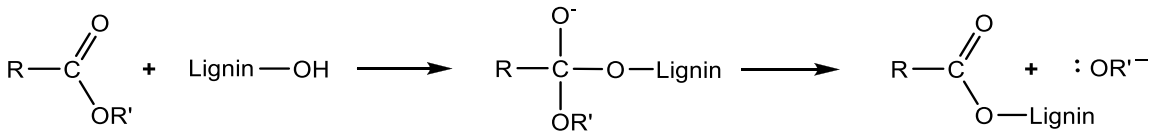


Fig. 9. Schematic diagram of the nucleophilic substitution of lignin hydroxyl groups with polyester polyol

Some notable observations can be made from the ^{31}P NMR spectra of the starting material (L2) and the lignins treated with polyester polyol (PL2) and PEG (L2+PEG). The ^{31}P NMR spectral analysis of the lignin treated with PEG confirmed the presence of a signal (triplet) at 147.1 ppm with a *J*-coupling constant of 10.73 Hz, which was due to the primary hydroxyl group of the PEG recorded in the aliphatic region of the treated lignin. The comparison of this signal with its original ^{31}P NMR spectrum showed slight changes in the chemical shift of the corresponding aliphatic hydroxyl groups. The primary hydroxyl group of the original PEG was recorded at 147.2 ppm (triplet) with a similar *J*-coupling constant of 10.73 Hz. The presence of a triplet signal with a similar coupling constant and different chemical shift for the treated lignin suggests the possibility of some physical or chemical interaction between the two precursors.

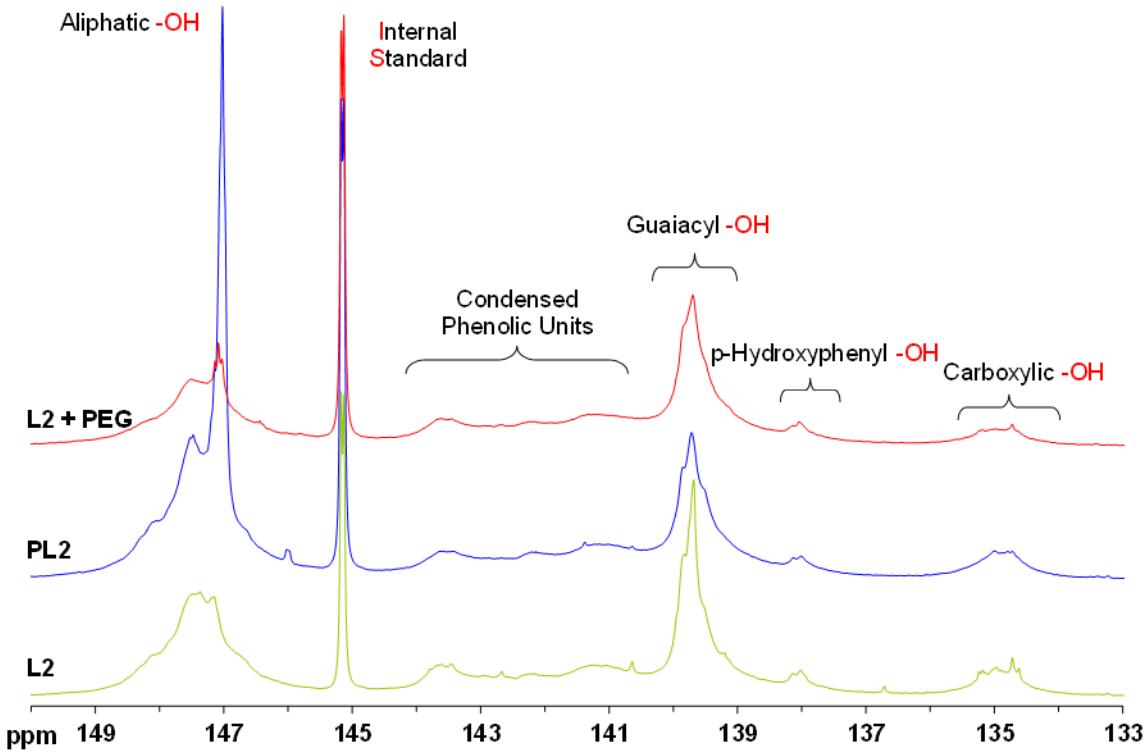


Fig. 10. ^{31}P NMR spectra and signal assignments of the Indulin AT before (L2) and after (PL2) treatment with polyester polyol and with PEG (L2+PEG) phosphitylated with TMDP

Further study showed that the intensity of such a signal was not as pronounced as the signals for its lignin counterpart treated with polyester polyol (PL2). Additionally, the ^{31}P NMR chemical shift for the lignin treated with PEG (L2+PEG) was recorded at 147.1 ppm, while the signal for the lignin treated with polyester polyol was recorded at 147.0 ppm. The difference in the chemical shift may have been due to the presence of oxygen in the polyester polyol and its deshielding effect on the ^{31}P NMR chemical shift.

Much like the lignins treated with polyester polyol, the content of several hydroxyl units in the treated lignin with PEG decreased considerably. The Size Exclusion Chromatography analysis of L2+PEG showed that the M_w increased from 7.69 to 50.25 kDa, and the M_n increased from 3.56 to 14.15 kDa. The hydroxyl content for several of the different lignin constituents before and after blending is reported in Table 3.

The FTIR spectra of the starting materials, Indulin AT (L2) and PEG, were compared with the blend (L2+PEG), and are presented in Fig. 11. The spectral analysis for the two sets of data showed noticeable differences in the lignin IR absorption bands before and after the blending process. The FTIR spectrum of the L2+PEG exhibited several new bands at different absorption frequencies between 2987 and 3071 cm^{-1} and at 1715, 1082, 870, and 694 cm^{-1}, which corresponded to the C-H stretching of methylene, H-bonded C=O, C-O alcohol of primary hydroxyl, out-of-plane C-H (aromatic) (Faix 1992), and etherified phenols (Ph-O-C), respectively. The presence of these new bands and shifts in frequency for the other bands suggested the occurrence of possible linkages between the lignin and PEG during the blending process.

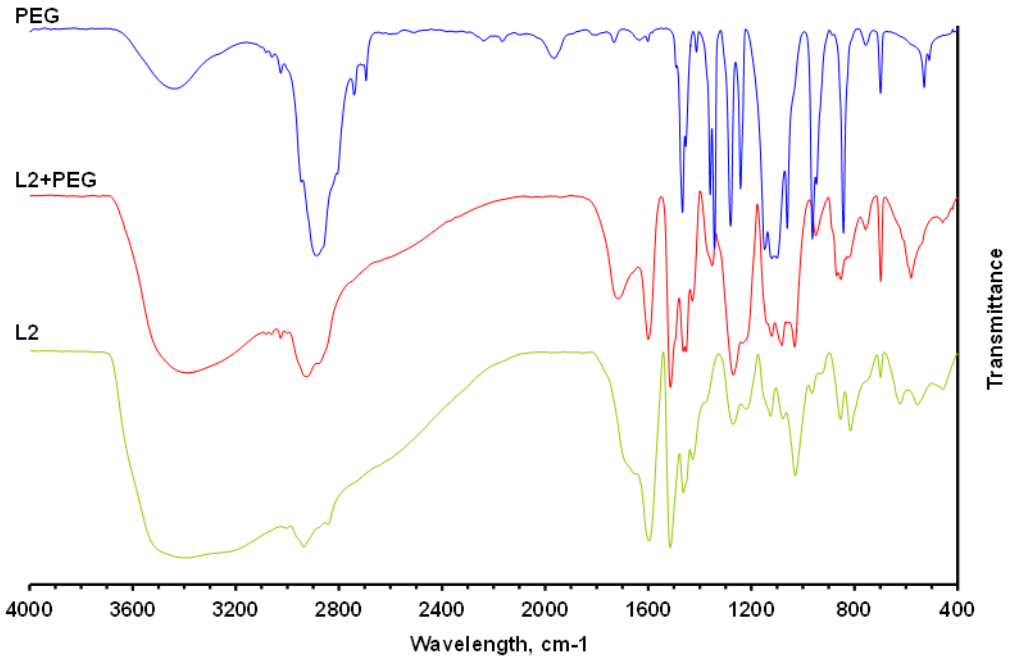


Fig. 11. FTIR spectra of the PEG and Indulin AT before (L2) and after treatment with PEG (PL2+PEG)

Table 3. Characterization of Indulin AT Before and After Treatment with Polyethylene Glycol by ^{31}P NMR Spectroscopy, Size Exclusion Chromatography, and Differential Scanning Calorimetry

Lignin Samples	L2	L2+PEG
^{31}P NMR Analysis (mmol/g)		
COOH	0.39	0.15
Non-condensed phenolic -OH		
G[a]	2.05	1.44
S[b]	0.00	0.00
H[c]	0.20	0.12
Condensed phenolic –OH	1.32	0.98
Aliphatic –OH	2.42	1.37
Total phenolic –OH	3.57	2.54
Total -OH	6.38	4.06
Size Exclusion Chromatography (Da × 10^3)		
M_w	7.69	50.25
M_n	3.56	14.15
d*n*/d*c*	0.208	0.193
M_w/M_n	2.16	3.55
Differential Scanning Calorimetry (°C)		
T_g	139	36, 107

a: guaiacyl -OH; b: syringyl -OH; c: p-hydroxyphenyl -OH

According to the ^{31}P NMR studies coupled with the size exclusion chromatography and FTIR analyses, the interaction between the lignin and PEG may have occurred in the manner illustrated in the schematic diagram in Fig. 12.

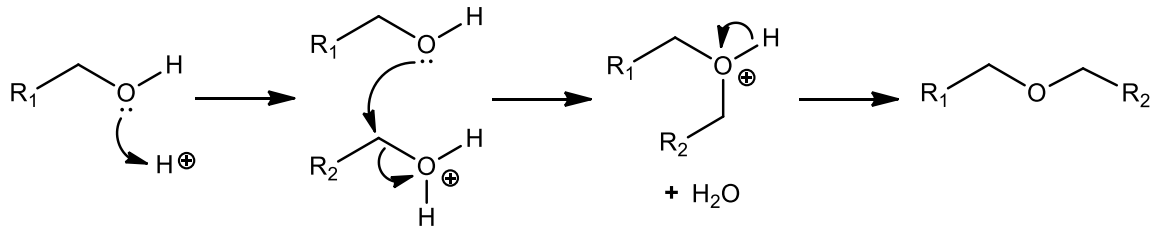


Fig. 12. Schematic diagram of the possible interaction of lignin hydroxyl groups with PEG

The physical properties of all four lignins treated with polyol and PEG were investigated by employing SEM as well as T_g measurements using DSC. The SEM images and morphology of each lignin before and after treatment with polyol are presented in Fig. 13. The comparison between the SEM images of the starting materials (L) and blends (PL) showed noticeable modifications to the lignin morphologies.

The SEM images of all of the starting materials (Fig. 13) showed that the average lignin particles were anywhere from 20 to 100 µm in size for L1, L3, and L4, and the particles were larger than 200 µm for L2. The subsequent blending with polyol (Fig. 13) altered their morphologies into densely packed porous microparticles with a sea-sponge-shaped structure in a relatively similar fashion for all of the blends, except for PL2, which had a plate-like flake morphology. In the case of L2, further Soxhlet extraction converted the morphology into coarser agglomerates, which was different from its predecessors. However, the SEM image of L2 treated with PEG was remarkably different from those blended with the polyester polyol. The L2+PEG image clearly showed well defined lignin particles, which averaged anywhere from 20 to 80 µm in size. The variation in the SEM images of the two sets of treatments for the same lignin (L2) with a similar recovery procedure directly showed the impact of the two polyol blends on the lignin.

The M_w and M_n distributions for both of the L1 and L4 agro-residue samples were found to be reduced after the blending process with polyol, while the d*n*/d*c* remained unaffected. The M_w for the L1 sample was lowered by 149.1 kDa, from 230.1 to 80.96 kDa, and the M_n decreased from 151.5 to 63.45 kDa. In the case of L4, the M_w was reduced from 253.8 to 110.34 kDa, and the M_n decreased from 172.5 to 97.57 kDa. The M_w/M_n values for both samples also decreased closer to unity. However, this was not the case for the L2 and L3 lignin samples. The M_w and M_n were determined to have increased considerably for both samples. The M_w and M_n for L2 increased from 7.69 to 13.95 kDa, and the M_n increased from 3.65 to 5.23 kDa. Similarly, the M_w for L3 was found to increase from 2.8 to 6.6 kDa, and the M_n increased from 0.62 to 1.80 kDa. The M_w/M_n value was determined to have increased slightly for L2, by 0.51, from 2.16 to 2.67, and decreased, by 0.85, for L3, from 4.52 to 3.67. The discrepancies between the L1 and L4 samples and the L2 and L3 samples may have been due to the type and origin of the lignins. The L1 and L4 lignins were both extracted from agricultural feedstock, while the L2 and L3 lignins were recovered from forestry biomass.

The T_g, which is an indirect measure of the crystallinity and degree of cross-linking, was determined in order to characterize the physical properties of the lignins before and after blending with polyols under similar conditions. The T_g measurements for the L1 to L4, L2+PEG, and PL1 to PL4 samples are reported in Table 1, Table 3, and

Table 4, respectively. The T_g analyses for the starting materials showed three distinct T_g values for the L1 sample, two values for the L4 sample, and a single value for the L2 and L3 samples. This was not surprising because both of the L1 and L4 lignin samples are known to be chemically modified by the supplier for greater compatibility as a substitute in lieu of petroleum-based polymers.

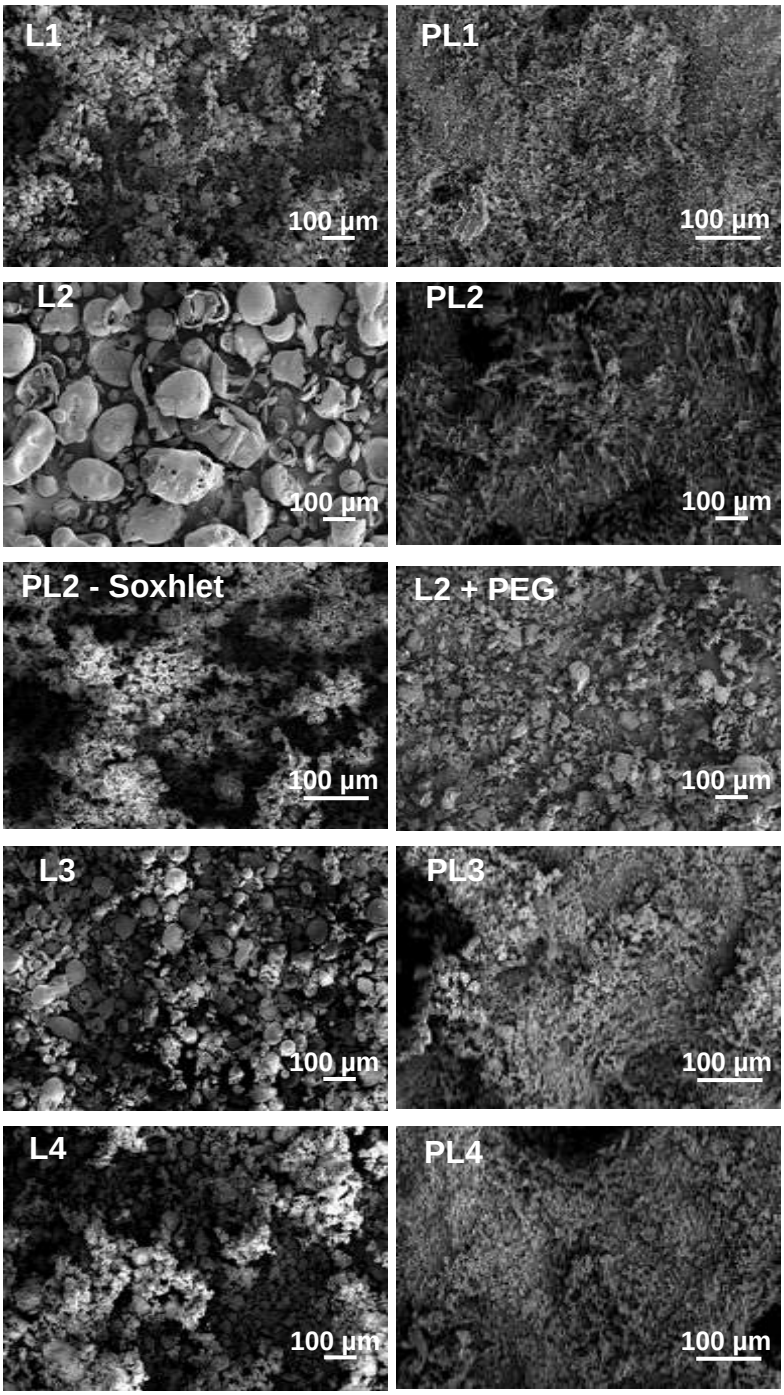


Fig. 13. SEM images of the lignins before (L1 to L4) and after (PL1 to PL4) treatment with polyol, after Soxhlet extraction (PL2 – Soxhlet), and after treatment with PEG (L2+PEG)

It is important to note that single T_g values implied complete compatibility between the components, while two or more T_g values suggested that the degree of miscibility was restricted. This was observed for the L2+PEG sample, where two different T_g values were detected at 36 and 107 °C. The lower magnitude of these temperatures compared with the T_g of L2 (139 °C) suggests that the lignin molecule had greater mobility after blending with PEG, even though its molecular weight increased noticeably.

Table 4. Characterization of the Lignin-Polyol Blends by Size Exclusion Chromatography and Differential Scanning Calorimetry

Parameters	PL1	PL2	PL3	PL4
Size Exclusion Chromatography (Da × 10^3)				
M_w	80.96	13.95	6.60	110.34
M_n	63.45	5.23	1.80	97.57
d*n*/d*c*	0.185	0.192	N/A	0.185
M_w/M_n	1.27	2.67	3.67	1.14
Differential Scanning Calorimetry (°C)				
T_g	82, 136	85, 134	131	115, 129

Much like L2+PEG, the T_g measurements for the subsequent lignin and polyol blends showed two distinct temperatures for PL1, PL2, and PL4, and a single T_g for the PL3 sample. All of the T_g values were relatively lower or the same as their starting materials, except for the PL3 sample. The T_g of the PL3 was determined to be 131 °C, which was 10 °C higher than the L3 sample. It was concluded that the T_g determination alone cannot provide direct evidence for the lignin-polyol interactions because the lignin T_g depends on a number of factors, such as molecular weight, amount of water, extent of hydrogen bonding, presence of carbohydrate impurities, chemical functionalization, and degree of branching in lignin polymeric chains.

The application of two-dimensional NMR can provide a much better basis for structural elucidation of lignin before and after blending with polyol. Specifically, HMQC experiments were performed to investigate the structural analysis and ^{1}H-^{13}C correlation (Kilpelaeinen *et al*. 1994; Ämmälahti *et al*. 1998; Capanema *et al*. 2004) of Indulin AT lignin before and after blending with polyester polyol. To distinguish physical mixtures from chemical interactions and to further establish any linkages that may have occurred during the blending process between the lignin and polyester polyol, additional experiments were performed. During a careful experiment, 1 g of polyol was blended with 0.5 g of lignin under similar conditions. After 3 d of mixing, the lignin and polyol were isolated according to the same procedure and then dried and weighed. The weights of the polyol and lignin were determined to be 1.04 g and 0.42 g, respectively, which corresponded to a 104% recovery for polyol, 84% recovery for lignin, and overall recovery of 97.3%. The mass balance between the starting and isolated materials suggested that ethyl acetate and diethyl ether as extracting solvents were efficient at removing excess polyol, and probably some soluble lignin residues as well. Despite the

polyol removal, the isolated Indulin AT (PL) displayed a sharp signal at 147.15 ppm in the aliphatic region caused by the presence of the aliphatic hydroxyl group of the polyol in the lignin. In the next step, 200 mg of the isolated lignin was subjected to the Soxhlet extraction procedure by utilizing 100 mL of ethyl acetate at 90 °C for a period of 4 h. The isolated materials were dried and measured, with the weights recorded as 28.8 mg for the yellow-brown viscous oil and 170.9 mg for lignin, which corresponded to a total recovery of 99.9%. The ^{31}P NMR spectral analysis for the oil fraction showed trace amounts of lignin moieties with the presence of guaiacyl units, and carboxylic acids found to be the most abundant. The presence of *p*-hydroxyl phenolic units was also discovered, and some condensed units, such as 5-5' biphenols and diaryl ether 4-O-5' units. Similarly, the ^{31}P NMR spectrum of the isolated lignin fraction revealed the presence of considerable amounts of polyol, which was recorded at 147.1 ppm.

The HMQC spectrum of the Indulin AT is presented in Fig. 14, where the ^{1}H-^{13}C correlations of the side-chain structures for a number lignin moieties were identified and labeled corresponding to the chemical structures shown in Fig. 15. The purpose of Fig. 15 was only to serve as a reference for comparison with the HMQC spectra of the lignin before and after the blending process, followed by their isolations with two subsequent extraction methods.

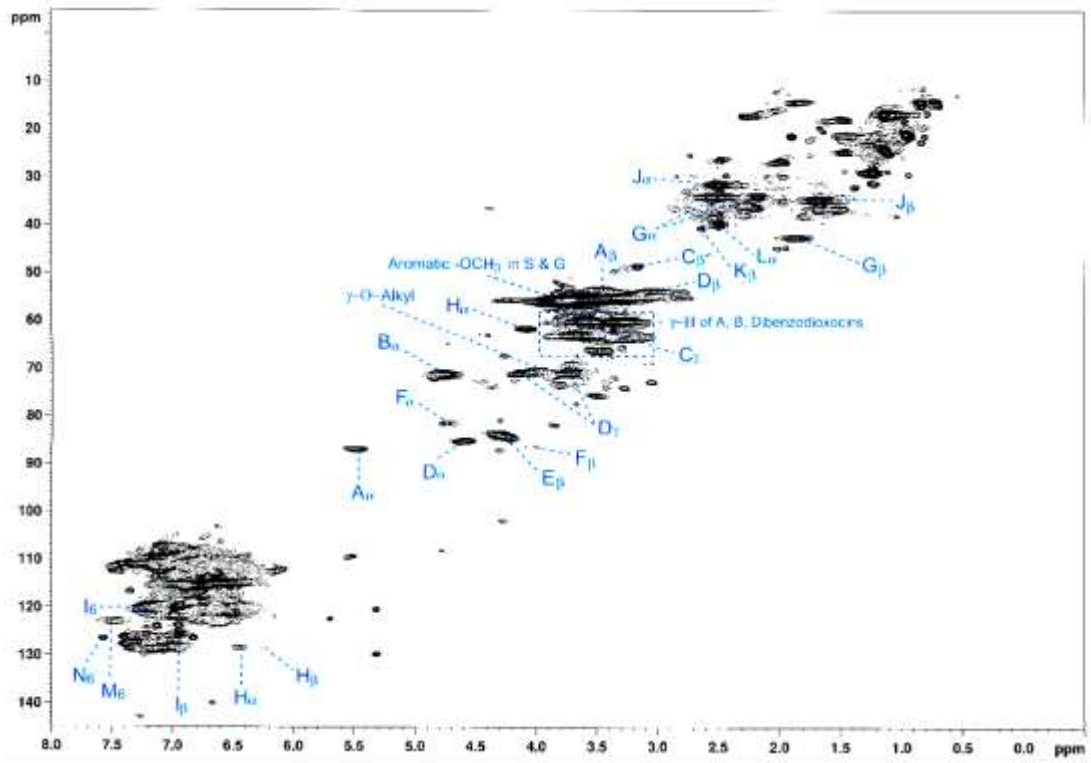


Fig. 14. HMQC spectrum of the Indulin AT

The HMQC spectra of the recovered lignin from the first isolation (blue) is superimposed over both the starting materials of polyester polyol (red) and Indulin AT (green), as presented in Fig. 16, which was expanded to show the upfield (a), midfield (b), and downfield (c) regions. In addition, the HMQC spectra of the lignin-polyol blend before (blue) and after Soxhlet extraction (black) is presented in Fig. 17 in a similar manner that shows the upfield (a), midfield (b), and downfield (c) regions. The HMQC

spectral analysis of the product from the first isolation showed signals that were exclusively caused by the presence of polyester polyol, as well as new signals caused by chemical linkages. These signals were detected even after Soxhlet extraction.

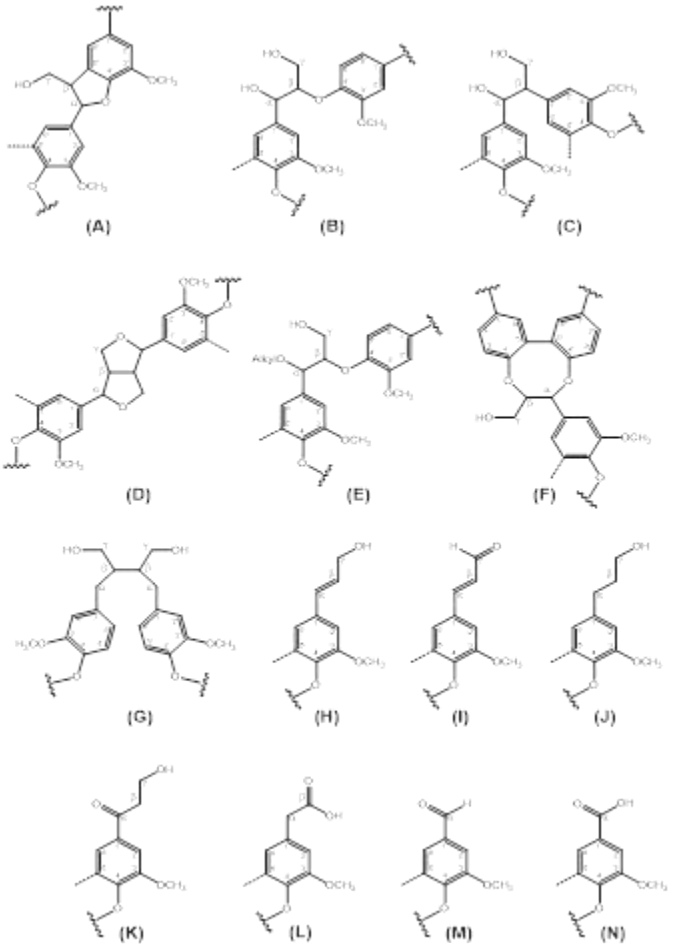
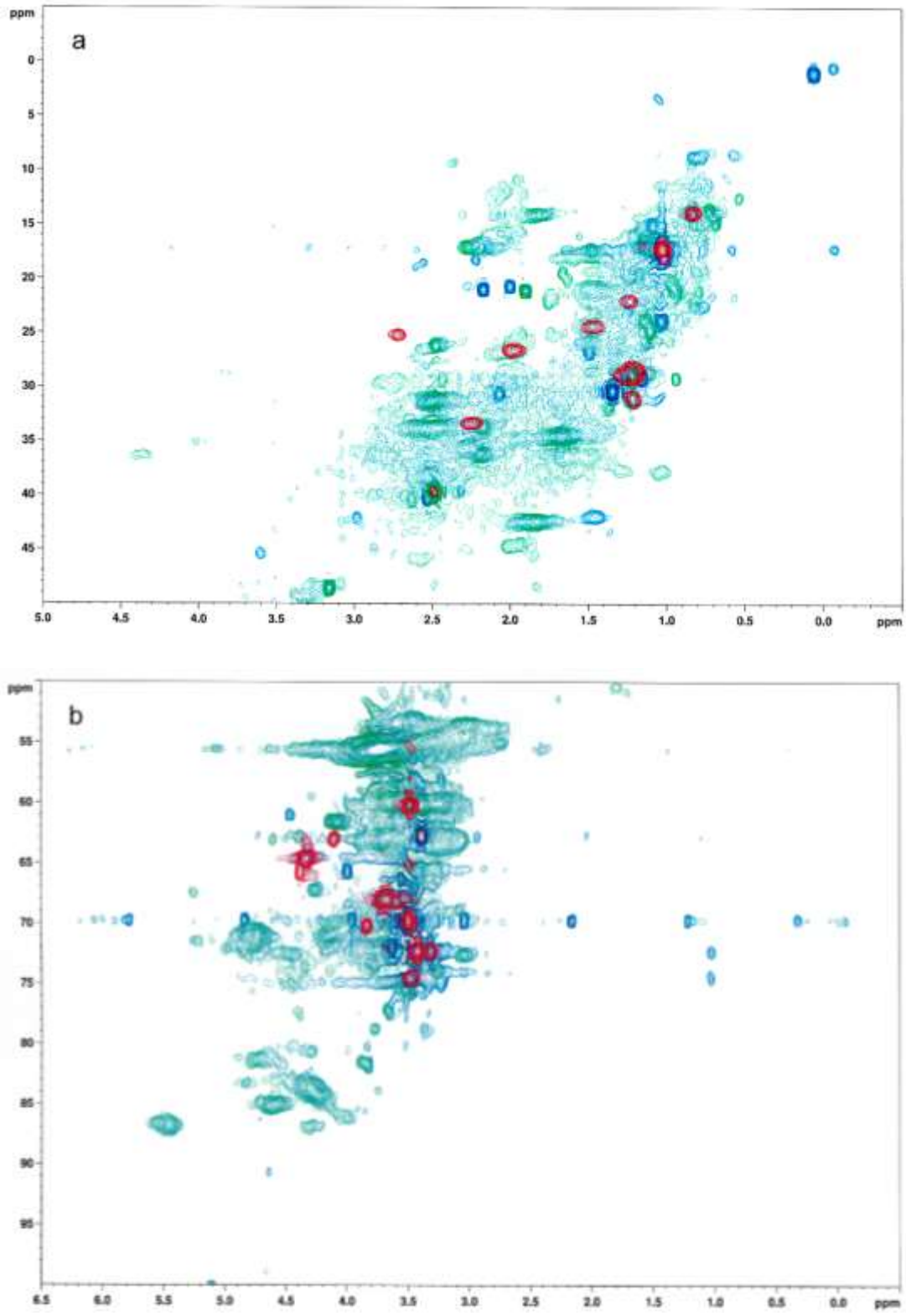


Fig. 15. Some structural units in Indulin AT lignin

The HMQC spectra of the polyol exhibited two sets of signals in the downfield region. The first set of four were recorded at 7.72/128.74, 7.68/128.66, 7.66/131.60, and 7.60/131.55 ppm, which were assigned to the C_3, C_6, C_1, and C_2 aromatic protons of the polyester polyols, respectively. This was confirmed by the ^{1}H NMR spectroscopic analysis of the Stepanpol PS2532, which seemed to contain a chemical structure that was similar to the *ortho*-phthalate-diethylene glycol-based aromatic polyester polyol. The other set of two signals recorded at 5.23/127.73 and 5.30/129.65 ppm were suspected to be H-C_α and/or H-C_β in the Ar-CH=CH-CH_2OH type structures. The HMQC spectrum of the Indulin AT lignin displayed signals that were similar to the latter and not at all similar to the former. Nevertheless, the presence of the first set of four signals due to the C_3, C_6 and C_1, C_2 aromatic protons of the polyester polyols were detected in the HMQC spectrum of the isolated products. These signals remained unaffected in the lignin even after extensive Soxhlet extraction. However, the latter signal assigned to $C_{Ar\text{-}H}$ disappeared after Soxhlet extraction. In addition, a number of other signals in this region, recorded at 7.64/130.27, 7.58/130.42, 7.48/129.72, 7.50/127.77, and more obviously, at 6.86/124.93 ppm, all disappeared after Soxhlet extraction. The elimination of these

signals may have indicated an affinity between the lignin and polyol, and the efficiency of the Soxhlet extraction. However, the presence of the remaining signals in the isolated lignin, which were exclusively assigned to the polyol, may have indicated the presence of linkages other than just physical interactions.



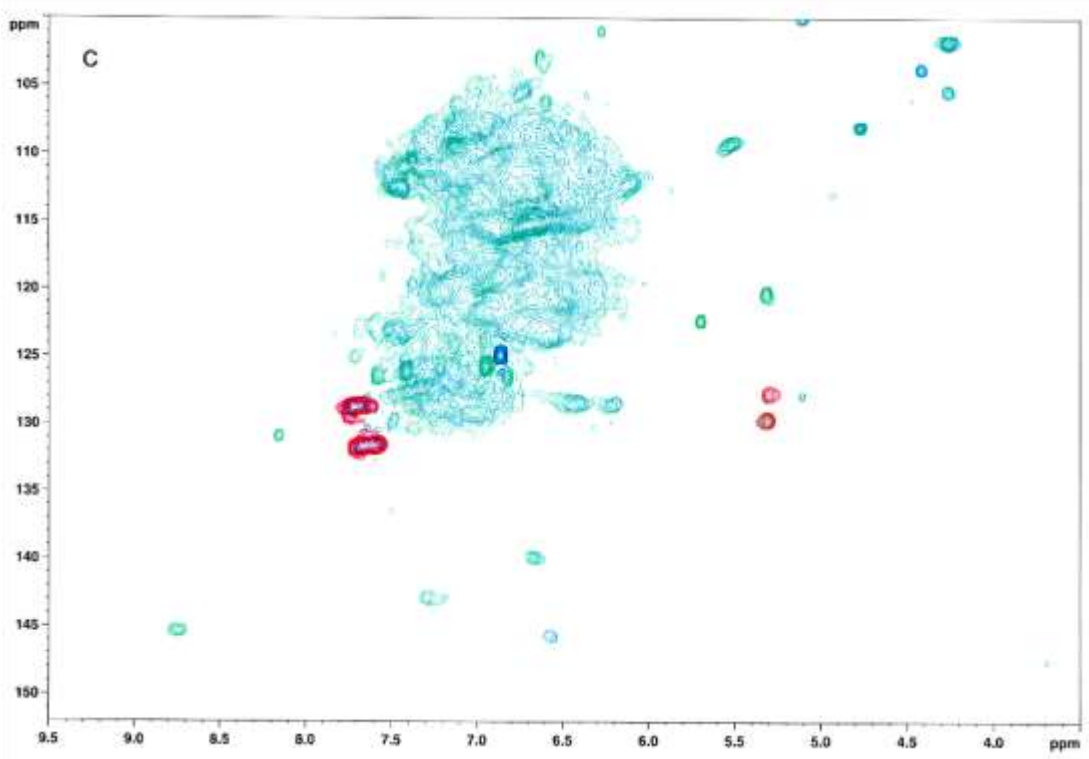
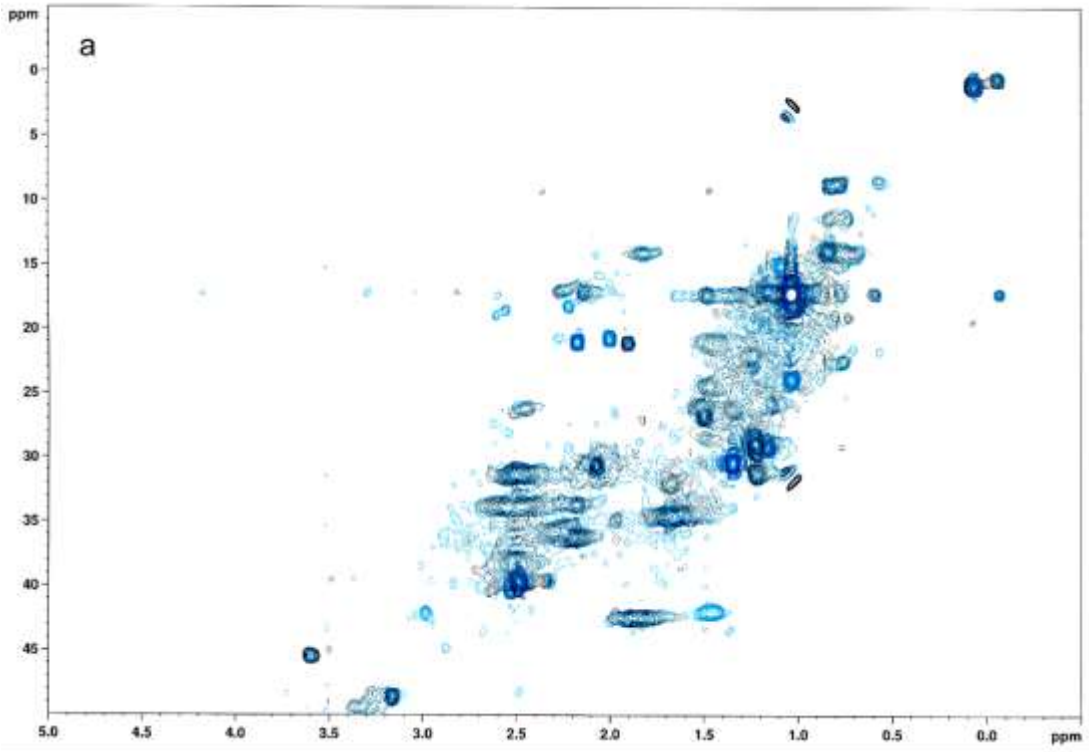


Fig. 16. HMQC spectra of the Indulin AT (green), polyester polyol (red), and lignin-polyol blend isolated by the first extraction (blue), where a is the upfield region, b is the midfield region, and c is the downfield region



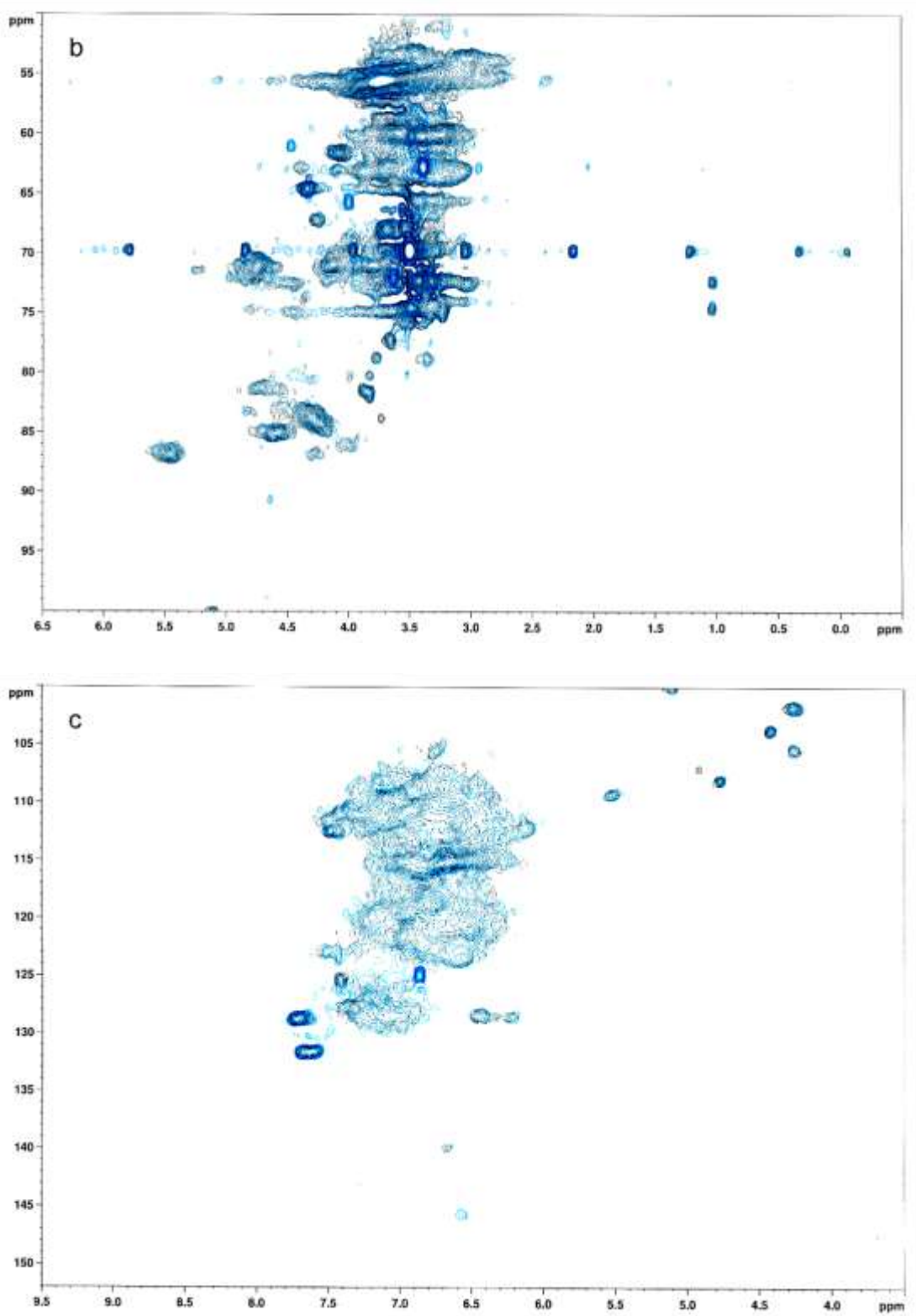


Fig. 17. HMQC spectra of the Indulin AT (black), polyester polyol (blue), and blend isolated by Soxhlet extraction, where a is the upfield region, b is the midfield region, and c is the downfield region

A similar trend was also observed in the midfield region of the HMQC spectra. This region is typically assigned to the H_α, H_β, and H_γ of the side-chain structures of several lignin moieties, such as arylglycerol-β-aryl ether structures, as well as the aromatic methoxyl groups of both the syringyl (S) and guaiacyl units in the lignin. Examination of the HMQC spectra of the isolated products indicated the absence of a polyol signal at 4.37/65.75 ppm after the first extraction, formation of a new signal at 3.99/65.68 ppm, and presence of a signal at 3.38/62.68 ppm that was eliminated after Soxhlet extraction. The formation of the new signal was suspected to have been caused entirely by either subsequent physical mixtures or by the presence of some impurities in either the lignin or polyol because it was removed after Soxhlet extraction. However, the majority of the polyol signals in this region were detected in the first extraction and Soxhlet extraction products. The most dominant signals were found at 4.33/64.62, 4.10/62.97, 3.83/70.21 (which was slightly shifted to 3.86/70.84 ppm after Soxhlet extraction), 3.68/67.99, 3.49/69.77, 3.48/65.11 (which was slightly shifted to 3.50/65.08 ppm after Soxhlet extraction), 3.48/60.17, 3.47/74.48, and 3.41/72.27 ppm. Apart from the removal of signals after Soxhlet extraction, the overall spectral comparison of this region between the first extraction and Soxhlet extraction were almost identical. A number of polyol signals were also detected in the upfield region of the HMQC spectra for the isolated lignin product. Signals at 2.25/3.32, 1.47/24.35, 1.23/22.0, 1.21/31.03, 1.21/28.64, 1.02/17.20, and 0.83/13.86 ppm were all detected in the first extraction and Soxhlet extraction products. Only two polyol signals, at 2.71/25.14 and 2.25/33.56 ppm, were not detected in any of the isolated products. The formation of three new signals was also recorded at 1.46/41.99, 1.34/30.38, and 1.03/23.85 ppm in the first extraction product. However, these signals were eliminated after Soxhlet extraction. Another notable observation in this region was the disappearance of a number of lignin signals after the first extraction process. The signals at 4.39/36.34, 4.34/36.29, 4.02/35.11, 3.82/28.73, 2.57/46.05, 2.31/14.03, in the region from 2.17/13.43 to 1.89/10.24, in the region from 2.06/43.8 to 1.82/46.11, 1.95/10.82, 1.91/12.25, 1.036/37.81, 0.94/29.22, and 0.54/12.54 ppm were originally detected in the starting material (Indulin AT). These signals may have been from some impurities in the lignin, which were then removed during the first extraction process by organic solvents.

CONCLUSIONS

1. The interaction between the lignin and polyol during the premixing stage of preparing a biobased PU was investigated by examining four different isolated lignins. Despite the extensive extractions of polyol by several organic solvents and Soxhlet procedure, the presence of polyols in all of the lignin samples was detected.
2. The presence of the polyol in the lignin, coupled with the physical and chemical characterizations of the isolated materials, strongly suggest the formation of ligno-polyols through both physical and chemical linkages.
3. The formation of ligno-polyols would benefit lignin manufacturers for partial substitution of petroleum-based polyols and also improves the reactivity of lignin in formulation of biobased PU.

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