Polyurethanes from Kraft Lignin without Using Isocyanates

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ABSTRACT: The reaction of a desulphurized kraft lignin with hexamethylene diamine and dimethyl carbonate has allowed the development of isocyanate-free polyurethane resins. The present research work is based on previous studies made with hydrolyzable and condensed tannins, but takes advantage of the higher number of hydroxyl groups present in lignin and their different aliphatic and aromatic character. The obtained materials were analyzed by Fourier transform infrared (FTIR) spectroscopy, matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry and solid-state cross-polarization/magic angle spinning (CP MAS) ^{13}C nuclear magnetic resonance (NMR), which have revealed the presence of urethane functions. The interpretation of the results has shown a larger number of species than when tannins were used and has indicated the presence of two types of bonds in the new molecules formed: ionic and covalent bonds.

KEYWORDS: Lignin, urethanes, non-isocyanate polyurethanes, MALDI-TOF, FTIR

1 INTRODUCTION

Polyurethanes can be prepared from a great variety of biorenewable polyols such as tannin [1–7] and lignin [8–11]. However, reaction of these biosourced polyols with polymeric isocyanates is still necessary to prepare polyurethanes. Alternate chemical routes for preparing non-isocyanate-based polyurethanes exist. These were pioneered by Rokicki and Piotrowska [12] and may involve vegetable oil-derived materials as polyols derived from renewable resources [13]. However, the use of vegetable oils in resins has been shown to present an unfavorable environmental balance, while the environmental balance of tannin-derived resins has been shown to be favorable [14].

Recently, polyurethanes without isocyanates based on hydrolyzable and condensed tannins have been prepared [15–17]. Tannins, mostly composed of natural polyphenolics, were reacted with dimethyl carbonate and hexamethylenediamine to prepare non-isocyanate polyurethanes. In this paper, the same approach to forming polyurethane bridges is applied to kraft lignin. The lignin is a very different polyphenolic material than tannin. The basic unit of lignin is a phenylpropane unit, which contains both aromatic and aliphatic hydroxyl groups instead of only aromatic hydroxyl groups as tannin. The aliphatic hydroxyl group is bonded to a saturated (sp^3) carbon in a chain, while the aromatic hydroxyl is bonded to an unsaturated (sp^2) carbon in the benzene ring. The benzene ring can stabilize a possible negative charge of the phenoxide ion through resonance because it is formed by sp^2 carbons, something which is more difficult in an aliphatic chain. This can lead to different behavior between aromatic and aliphatic hydroxyls in the preparation of isocyanate-free polyurethanes with kraft lignin.

2 EXPERIMENTAL

2.1 Sample Preparation

The commercial lignin used was a desulphurized softwood kraft lignin, namely BioChoice™ kraft lignin supplied by Domtar Inc. (Montreal, Quebec, Canada) from their Plymouth, North Carolina mill (USA). Dimethyl carbonate 99% (DMC) was obtained from Acros Organics (Geel, Belgium), and hexamethylenediamine technical grade 70% (HMDA) from Aldrich Chemical Co. Inc. (Milwaukee, USA).

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The samples were prepared as follows, without applying any purification steps to any of the reagents:

1. In the first method, 10 g of lignin powder was mixed and stirred for two hours with 22 g of dimethyl carbonate (DMC) at room temperature. Then, 8 g of hexamethylenediamine (HMDA) was added to the mixture and stirred. The mixture was divided into four samples, which were kept at room temperature and at 80 °C, 103 °C and 180 °C in an oven for 24 hours. These samples have been called LDH-X, where X is the temperature at which the sample was reacted.

2. In the second method, 8 g of lignin powder and 8 g of HMDA were mixed and placed in an oven at 60 °C for 18 hours. The mixture was then divided into four parts. To each part, half of its weight was added as weight of DMC. The samples were placed at room temperature and in ovens at 80 °C, 103 °C and 180 °C for 24 hours. These samples have been called LHDWpH-X, where X is the temperature at which the sample was reacted.

3. In the third method, 8 g of lignin powder and 8 g of HMDA, which was previously mixed with 1.5 g of 33% NaOH in water, were mixed and placed in an oven at 60 °C for 18 hours. The mixture was then divided into four parts. To each part, half of its weight was added as weight of DMC. The samples were placed at room temperature and in ovens at 80 °C, 103 °C and 180 °C for 24 hours. The samples have been called LHDpH-X, where X is the temperature of the sample.

All the samples were prepared in open containers and in a non-neutral-gas-blanketed oven. The samples were then stored in an Eppendorf tube sealed with parafilm inside of a desiccator. The samples were characterized as formed.

The samples obtained by reacting at 180 °C were solids, the samples obtained by reacting at 103 °C were hard pastes and the remaining ones were viscous liquids.

2.2   Coating Samples

The samples of lignin-based urethanes were tested for coating application on the surface of beech wood. The samples were prepared as described in the experimental section. However, after the addition of HMDA in the LDH formulation and the addition of DMC in the formulations of LHDWpH and LHDpH, the samples were heated one hour in an oven at 60 °C to obtain homogeneous viscous liquids, which quickly became pastes as the temperature decreased. The viscous liquids were then spread over the wood surface with a spatula, with a load of around 1–2 kg/m². The coated wood samples were put in an oven preheated at 180 °C and were covered with a silicone sheet. A metal plate was placed over the samples with 3 kg of weight over it to apply pressure. The coated wood samples were left for one hour at 180 °C before cooling.

2.3   Analysis

2.3.1   FTIR

To confirm the presence of urethane structures, Fourier transform infrared (FTIR) analysis was carried out using a Shimadzu IRAffinity-1 spectrophotometer. A blank sample tablet of potassium bromide, ACS reagent from Acros Organics, was prepared for the reference spectrum. A similar tablet was prepared by mixing potassium bromide with 5% w/w of the sample powder for analysis. The spectrum was obtained in absorbance measurement by combining 32 scans with a resolution of 2.0. The reference DMC spectrum can be obtained [18].

2.3.2   MALDI-TOF

Samples for matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis were prepared by first dissolving 5 mg of sample powder in 1 mL of a 50:50 v/v acetone/water solution. Then 10 mg of this solution was added to 10 µL of a 2,5-dihydroxy benzoic acid (DHB) matrix. The locations dedicated to the samples on the analysis plaque were first covered with 2 µL of a NaCl solution of 0.1 M in 2:1 v/v methanol/water, and predried. Then 1 µL of the sample solution was placed on its dedicated location and the plaque was dried again. MALDI-TOF spectra were obtained using an AXIMA Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK) using a linear polarity-positive tuning mode. The measurements were carried out making 1000 profiles per sample with 2 shots accumulated per profile. The spectrum precision was +1Da.

2.3.3   CP-MAS ^{13}C NMR

Solid-state CP-MAS (cross-polarization/magic angle spinning) ^{13}C NMR spectra of the solid samples obtained by the different methods at 180 °C were recorded on a Bruker MSL-300 spectrometer at a frequency of 75.47 MHz. Chemical shifts were calculated

relative to tetramethyl silane (TMS). The rotor was spun at 4 kHz on a double-bearing 7 mm Bruker probe. The spectra were acquired with 5 s recycle delays, a 90° pulse of 5 ms and a contact time of 1 ms. The number of transients was 3000.

2.3.4 Contact Angle

The contact angle of the treated surfaces at one minute from the water drop being placed on it with a syringe was measured with an EasyDrop contact angle apparatus, using drop shape analysis software (Krüs GmbH, Hamburg, Germany). Untreated wood was used as control.

3 RESULTS AND DISCUSSION

3.1 MALDI-TOF

In Tables 1, 2 and 3 are shown the interpretation of the peaks of the MALDI-TOF analysis of the reaction products obtained for the LDH (Fig. 1a,b), LHDWpH and LHDpH at 180 °C, thus for the cases in which the reaction was more complete. A number of species are noticeable but what is of interest is the presence of urethane linkages obtained by the different reactions occurring. Thus, chemical species formed by the reaction of the diamine with the aliphatic hydroxyl group of a lignin unit according to a reaction already described [19] have then reacted with dimethylcarbonate to form a urethane group between the latter and the diamine. This is shown by the peak at 361 Da from the LHDWpH spectrum at 180 °C, as follows:
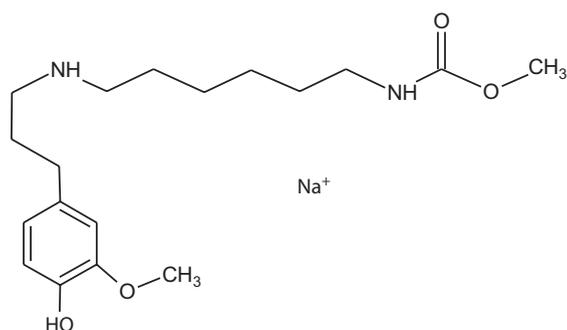
361 Da

Similar species of urethane linkages between diamine and dimethyl carbonate, but where an ionic bond has formed between one of the amino groups of the diamine and an aliphatic hydroxyl group of a lignin unit, also occur as the peak at 441 Da from LHDWpH at 103 °C, as follows:
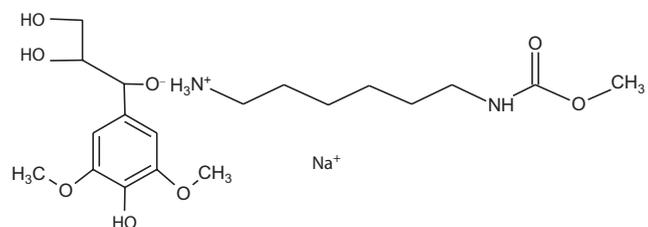
441 Da

The more significant types of compounds are, however, those where the urethane linkages are formed between the carbonate prereacted on lignin units and the diamine leading to oligomers and crosslinking in this manner between lignin chains. An example of this type of urethane linkage is shown by the peak at 555 Da from LDH at 180 °C.
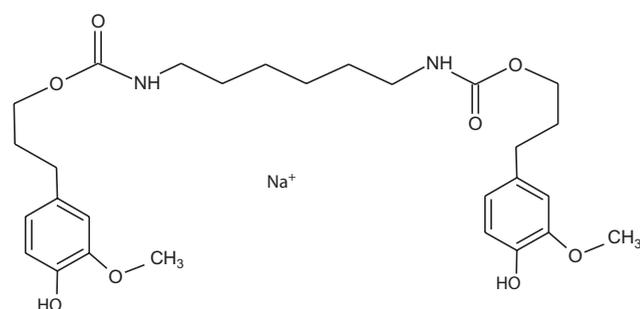
555 Da

Equally, urethane linkages in chemical species formed by reaction of the diamine with the dimethyl carbonate prereacted with the phenolic hydroxyl groups of lignin units do occur, as indicated by the peak at 361 Da from the spectrum of LDH at 180 °C.
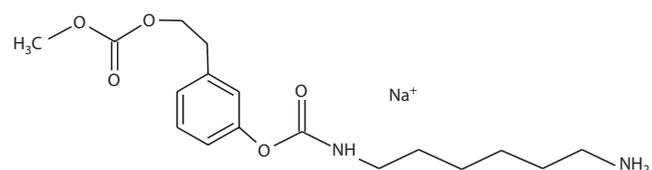
361 Da

3.2 FTIR

Figure 2 shows the FTIR spectrum of the unmodified, unreacted, original lignin, and Figure 3 shows the product of the reaction of lignin with DMC at ambient temperature. On these two figures can be seen [20]:

- The band at 1745 cm^{-1} belonging to C=O stretching in the ester group of dimethylcarbonate (DMC) (Figure 3).

Table 1 MALDI-TOF analysis of oligomer species formed in the reaction of kraft lignin with dimethyl carbonate and hexamethylenediamine at 180 °C. Case LDH.

Peak in spectrum (Da)	Oligomer type	Calculated peak (Da)
137,6	Lignin	
255,5	DMC-138Lig-DMC	254
	198Lig-DMC	256
301,6	138Lig-DMC-138Lig	302
327,7	138Lig=DMCx2=138Lig	328
339,5	198Lig-DMC-U-HMDA	340
358,7	DMC-274Lig=DMC	358
360,5	DMC-138Lig-DMC-138Lig	360
361,5	DMC-138Lig-DMC-U-HMDA+Na	361
	138Lig-DMC-198Lig	362
366,7	138Lig-DMC-179Lig+Na	366
376,4	138Lig-DMC-154Lig-DMC	376
386,7	305Lig-DMC+23	386
413,5	DMC-274Lig-DMC+Na	413
441,7	HMDA-U-DMC-274Lig=DMC	442
443,7	DMC-198Lig-DMC-U-HMDA+Nax2	444
	HMDA-U-DMC-138Lig-DMC-138Lig	444
465,7	HMDA-U-DMC-182Lig-DMC-U-HMDA	466
	HMDA-U-DMC-274Lig=DMC+Na	465
479,7	HMDA-U-DMC-198Lig-DMCx2+Nax2	479
493,8	305Lig-DMC-U-HMDA+Nax2	493
537,4	154Lig-DMC-154Lig-DMC-154Lig+Na	537
538,3	DMC-198Lig-DMC-198Lig-DMC	538
543,6	154Lig-DMC-U-HMDA-U-DMC-180Lig+Na	543
	178Lig-DMC-U-HMDA-U-DMC-198Lig	544
551,3	198Lig-DMC-305Lig+Na	552
556,6	182Lig-DMC-U-HMDA-U-DMC-182Lig+Na	555
	154Lig-DMC-138Lig-DMC-154Lig-DMC	556
573,4	DMC-138Lig-DMC-138Lig-DMC-138Lig-DMC+Na	573
	274Lig-DMC-274Lig	574
593,8	154Lig-DMC-U-HMDA-U-DMC-272Lig	594
608	198Lig-DMC-U-HMDA-U-DMC-242Lig	608
621,8	DMC-198Lig-DMC-198Lig-DMC-U-HMDA	622
639,4	HMDA-U-DMC-274Lig-(DMC)-DMC-U-HMDA+Na	639
	154Lig-DMC-138Lig-DMC-154Lig-DMC-U-HMDA	640
673,2	180Lig-DMC-U-HMDA-U-DMC-326Lig	674
713,2	DMC-274Lig-DMC-274Lig-DMC+Na	713
	138Lig-DMC-179Lig-DMC-179Lig-DMC-U-HMDA+Na	713
	272Lig-DMC-U-HMDA-U-DMC-272Lig	712
735,3	138Lig-DMC-179Lig-DMC-179Lig-DMC-U-HMDA+Nax2	736
763,5	HMDA-U-DMC-138Lig-DMC-138Lig-DMC-138Lig-DMC-U-HMDA+Nax2	764

U = urethane linkage; DMC = dimethyl carbonate; HMDA = hexamethylenediamine; 138 lignin = lignin fragment of 138 molecular weight; 198 lignin = lignin fragment of 198 molecular weight

Table 2 MALDI-TOF analysis of oligomer species formed in the reaction of kraft lignin with dimethyl carbonate and hexamethylenediamine at 180 °C. Case LHDWpH.

Peak in spectrum (Da)	Oligomer type	Calculated peak (Da)
137,8	Lignin	
198	Lignin	
279,6	182Lig-HMDA	280
316,8	138Lig-HMDA-U-DMC+Na	317
335	HMDA+-104+-HMDA	336
333,7	HMDA-138-HMDA	334
335,7	138Lig+-HMDA-U-DMC+Na	335
	138Lig+-HMDA-U-DMC+Na	335
	156Lig-HMDA-U-DMC+Na	335
338,8	182Lig-HMDA-U-DMC	338
344,8	104Lig-HMDA-138Lig+Na	345
352,8	156Lig+-HMDA-U-DMC+Na	353
357,7	HMDA-138Lig-HMDA+Na	357
358,8	242Lig+-HMDA	358
	138Lig+-HMDA-U-DMC+Nax2	358
	156Lig-HMDA-U-DMC+Nax2	358
361,6	182Lig-HMDA-U-DMC+Na	361
378	HMDA-182Lig-HMDA	378
392,8	HMDA-138-HMDA-U-DMC	392
400	198Lig-HMDA-U-DMC+Nax2	400
414,9	HMDA-138-HMDA-U-DMC+Na	415
	HMDA-138Lig-HMDA-U-DMC+Na	415
443,8	Lignin	
	182Lig-HMDA-182Lig	444
	244Lig+-HMDA-U-DMC+Na	441
450,8	DMC-U-HMDA-138-HMDA-U-DMC	450
451,9	DMC-U-HMDA+-104+-HMDA-U-DMC	452
458	HMDA-182Lig-HMDA-U-DMC+Na	459
475,8	DMC-U-HMDA+-104+-HMDA-U-DMC+Na	475
495	198Lig-HMDA+-198Lig	494
537,5	138Lig-HMDA-U-DMC-U-HMDA-154Lig+Na	537
	138Lig-HMDA-U-DMC-U-HMDA-178Lig	538
543,9	HMDA-242Lig-HMDA-U-DMC+Nax2	542
551	HMDA-138Lig-HMDA-138Lig-HMDA	552
556,8	HMDA+-104Lig+-HMDA+-104Lig+-HMDA	556
559,6	154Lig-HMDA-U-DMC-U-HMDA-182Lig	558
	182Lig-HMDA-182Lig-O-+HMDA	560
	182Lig-HMDA-182Lig+-HMDA	560
576,9	178Lig-HMDA-U-DMC-U-HMDA-154Lig+Na	577
	DMC-U-HMDA-242Lig-HMDA-U-DMC+Na	577

(Continued)

Table 2 Cont.

Peak in spectrum (Da)	Oligomer type	Calculated peak (Da)
600,2	242Lig+-HMDA+-242Lig	600
	DMC-U-HMDA-242Lig-HMDA-U-DMC+Nax2	600
602,9	182Lig-HMDA-U-DMC-U-HMDA-198Lig	602
608	HMDA+-272+-HMDA-U-DMC+Na	608
610	198Lig+-HMDA+-198Lig-HMDA	610
	198Lig+-HMDA+-180Lig+-HMDA	610
	HMDA-138Lig-HMDA-138Lig-HMDA-U-DMC	610
622	178Lig-HMDA-U-DMC-U-HMDA-198Lig+Na	621
636,1	180Lig-HMDA-180Lig-O-+HMDA-U-DMC+Na	637
	HMDA+-104Lig+-HMDA+-104Lig+-HMDA-U-DMC+Na	637
	180Lig-HMDA-180Lig+-HMDA-U-DMC+Na	637
	180Lig-HMDA-180Lig+-HMDA-U-DMC+Na	637
713,3	HMDA+-180Lig-HMDA-180Lig-HMDA	712
735,2	HMDA+-180Lig-HMDA-180Lig-HMDA	735
764,2	DMC-U-HMDA+-138Lig+-HMDA+-138Lig+-HMDA-U-DMC+Na	763
875,4	DMC-U-HMDA-242Lig-HMDA-242Lig-HMDA-U-DMC	876
	326Lig-HMDA-U-DMC-U-HMDA-326Lig	874
891,7	DMC-U-HMDA-180Lig-HMDA-156Lig-HMDA-180Lig-HMDA-U-DMC	890

U = urethane linkage; DMC = dimethyl carbonate; HMDA = hexamethylenediamine; 104, 138, 154, 178, 182, 198, 326 lignin = lignin fragments of respectively 104, 138, 154, 178, 182, 198, 326 molecular weight

Table 3 MALDI-TOF analysis of oligomer species formed in the reaction of kraft lignin with dimethyl carbonate and hexamethylenediamine at 180 °C. Case LHDpH.

Peak in spectrum (Da)	Oligomer type	Calculated peak (Da)
137,8	Lignin	
198	Lignin	
278,7	138Lig+-HMDA+Na	277
	156Lig-HMDA+Na	277
279,6	182Lig-HMDA	280
316,7	138Lig-HMDA-U-DMC+Na	317
330,7	156Lig+-HMDA-U-DMC	330
358,7	HMDA-138Lig-HMDA+Na	357
	242Lig+-HMDA	358
	138Lig+-HMDA-U-DMC+Nax2	358
	156Lig-HMDA-U-DMC+Nax2	358
361,6	182Lig-HMDA-U-DMC+Na	361
379,6	HMDA-182Lig-HMDA	378
400,6	180Lig+-HMDA-U-DMC+Nax2	400
	198Lig-HMDA-U-DMC+Nax2	400
441,7	244Lig+-HMDA-U-DMC+Na	441
443,8	182Lig-HMDA-182Lig	444

(*Continued*)

Table 3 Cont.

Peak in spectrum (Da)	Oligomer type	Calculated peak (Da)
451	DMC-U-HMDA-138-HMDA-U-DMC	450
	DMC-U-HMDA+-104+-HMDA-U-DMC	452
457,7	HMDA-180Lig-HMDA-U-DMC+Na	457
469,7	HMDA+-156Lig+-HMDA-U-DMC+Na	469
472,8	DMC-U-HMDA-138-HMDA-U-DMC+Na	473
	DMC-U-HMDA-138Lig-HMDA-U-DMC+Na	473
494,7	DMC-U-HMDA-182Lig-HMDA-U-DMC	494
494,7	198Lig-HMDA+-198Lig	494
	156Lig-HMDAx2-156Lig+Na	495
537,4	138Lig-HMDA-U-DMC-U-HMDA-154Lig+Na	537
	138Lig-HMDA-U-DMC-U-HMDA-178Lig	538
551	HMDA-138Lig-HMDA-138Lig-HMDA	552
	DMC-U-HMDA-242Lig-HMDA-U-DMC+Na	577
602,8	138Lig-HMDA-U-DMC-U-HMDA-242Lig	602
	178Lig-HMDA-U-DMC-U-HMDA-180Lig+Na	603
607,8	HMDA+-272+-HMDA-U-DMC+Nax2	608
613,9	180Lig-HMDA-180Lig-O-+HMDA-U-DMC	614
	HMDA+-104Lig+-HMDA+-104Lig+-HMDA-U-DMC	614
	180Lig-HMDA-180Lig+-HMDA-U-DMC	614
621,8	178Lig-HMDA-U-DMC-U-HMDA-198Lig+Na	621
633,8	HMDA-138Lig-HMDA-138Lig-HMDA-U-DMC+Na	633
642,8	DMC-U-HMDA+-272+-HMDA-U-DMC+Na	643
	178Lig-HMDA-U-DMC-U-HMDA-242Lig	642
647,8	272Lig-HMDA-U-DMC-U-HMDA-154Lig	648
704	DMC-U-HMDA+-138Lig-HMDA-138Lig+-HMDA-U-DMC	704
727,7	DMC-U-HMDA+-138Lig-HMDA-138Lig+-HMDA-U-DMC+Na	727
	DMC-U-HMDA-156Lig-HMDA-156Lig-HMDA-U-DMC+Na	727
	DMC-U-HMDA+-138Lig-HMDA-138Lig+-HMDA-U-DMC+Na	727
735	HMDA+-180Lig-HMDA-180Lig-HMDA-U-DMC+Na	735
741	DMC-U-HMDA+-138Lig+-HMDA+-138Lig+-HMDA-U-DMC	740
763,9	DMC-U-HMDA+-138Lig+-HMDA+-138Lig+-HMDA-U-DMC+Na	763
789,9	198Lig+-HMDA-198Lig-HMDA+-198Lig	790
	198Lig-HMDA+-180Lig+-HMDA+-198Lig	790
	HMDA+-180Lig+-HMDA+-180Lig+-HMDA-U-DMC+Na	789
	HMDA-198Lig+-HMDA+-198Lig-HMDA-U-DMC+Na	789
	HMDA+-198Lig+-HMDA+-180Lig+-HMDA-U-DMC+Na	789
	272Lig-HMDA-U-DMC-U-HMDA-272Lig+Na	789
	242Lig-HMDA-U-DMC-U-HMDA-326Lig	790
829,7	DMC-U-HMDA+-180Lig+-HMDA-180Lig-HMDA-U-DMC+Na	829
	DMC-U-HMDA-198Lig-HMDA-198Lig+-HMDA-U-DMC+Na	829
	DMC-U-HMDA+-198Lig-HMDA-180Lig+-HMDA-U-DMC+Na	829

U = urethane linkage; DMC = dimethyl carbonate; HMDA = hexamethylenediamine; 138, 156, 178, 182, 198, 242 lignin = lignin fragments of respectively 138, 156, 178, 182, 198, 242 molecular weight

Data: LDH180_iongateOff0001.B2[c] 17 Mar 2017 14:28 Cal: cal 17 Mar 2017 13:30
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 75, P.Ext. @ 2300 (bin 78)

%Int.   384 mV[sum= 76802 mV] Profiles 1-200 Smooth Av 50 -Baseline 150
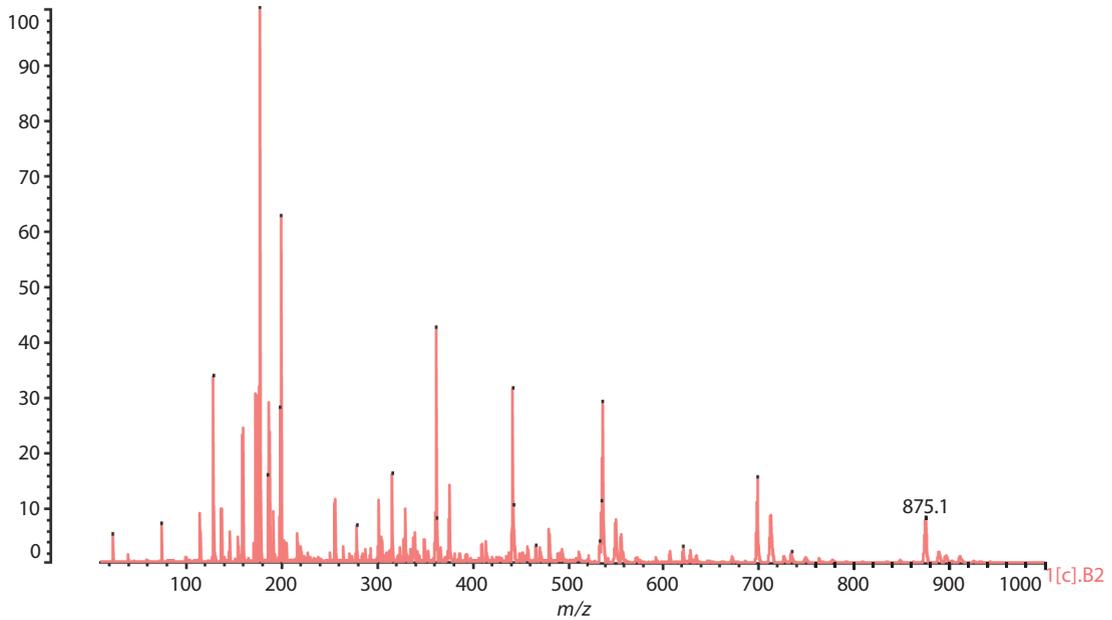
Data: LDH180_iongateOff0001.B2[c] 17 Mar 2017 14:28 Cal: cal 17 Mar 2017 13:30
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 75, P.Ext. @ 2300 (bin 78)

%Int.   16 mV[sum= 3153 mV] Profiles 1-200 Smooth Av 50 -Baseline 150
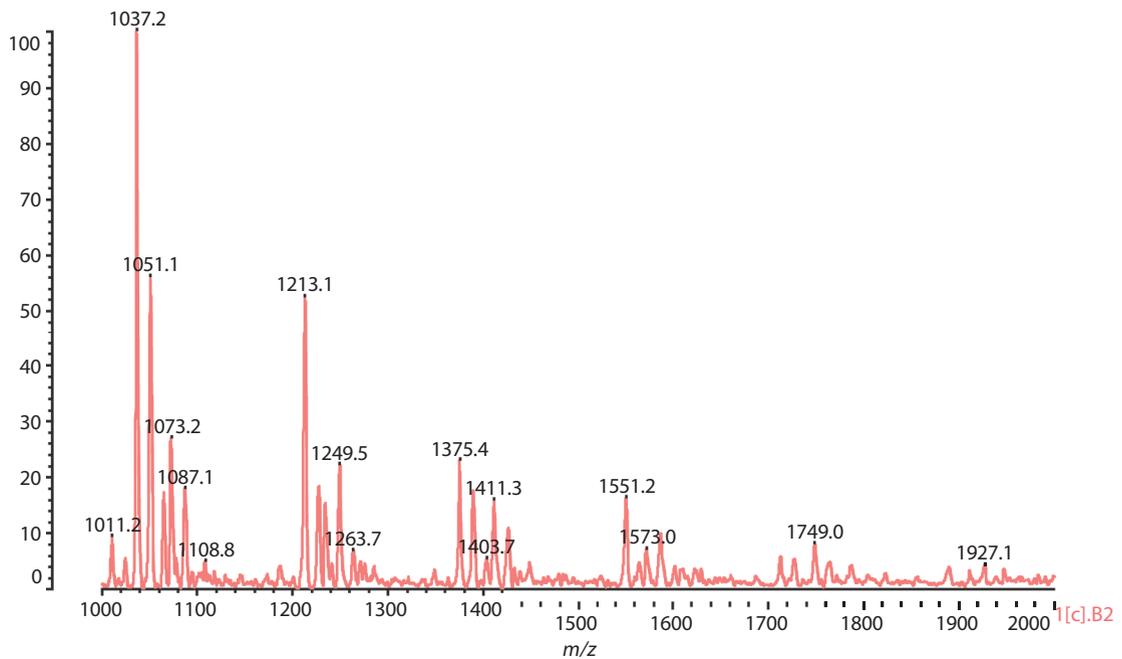
Figure 1 MALDI-TOF of the reaction products for the reaction LDH at 180 °C of lignin to form non-isocyanate polyurethanes: (**a**) 10 Da – 1000 Da range, (**b**) 1000 Da – 2000 Da range.

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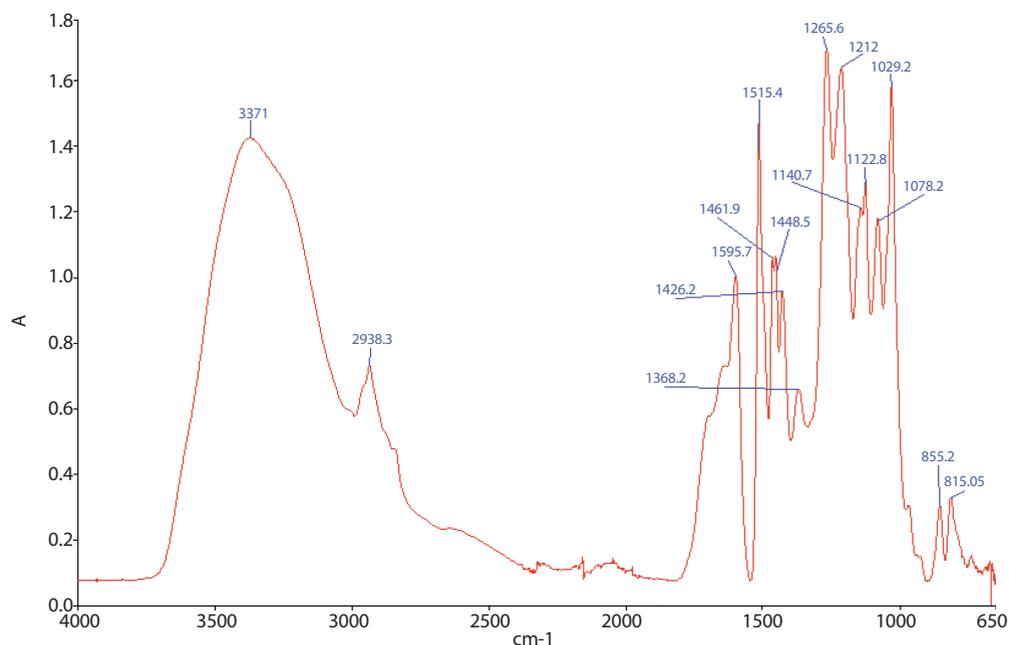
Figure 2 FTIR of unreacted lignin.
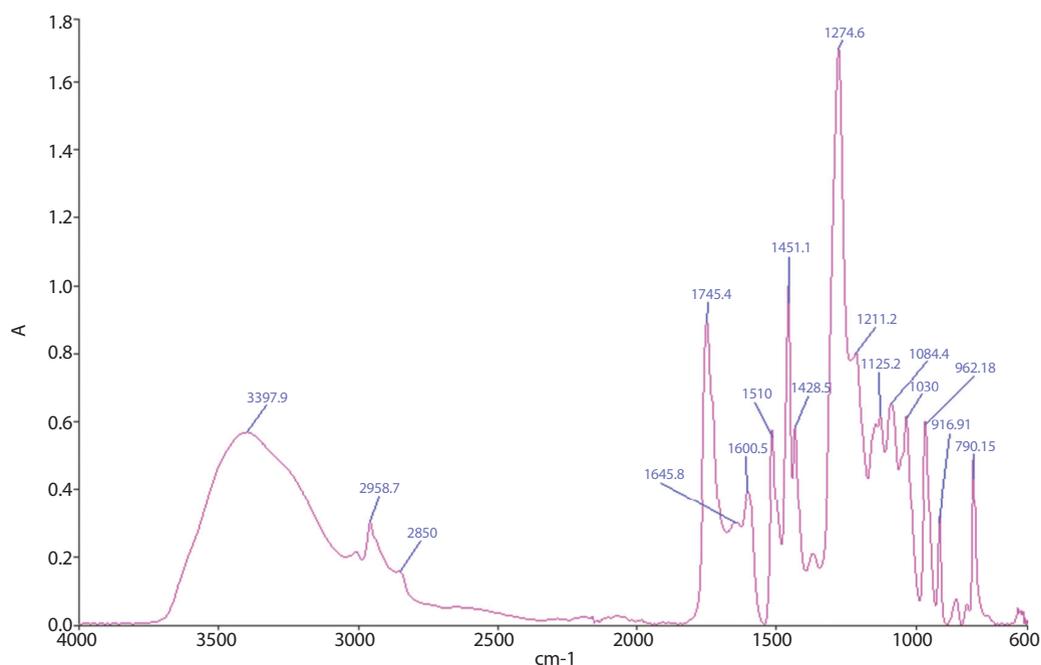
Figure 3 FTIR of the reaction of lignin with dimethyl carbonate at ambient temperature.

- The band at 1645 cm^{-1} belonging to the C=O stretching in lignin, this peak appearing as one of the shoulders of the peak at 1595 cm^{-1} peak in unreacted lignin (Figure 2).
- The band at 1451 cm^{-1} belonging to the asymmetric C-H deformation in –CH$_3$ and –CH$_2$, and the aromatic skeleton plus the C-H deformation in CH$_3$ from DMC (Figure 3).

- The band at 1274 cm^{-1} belonging to C-O stretching in the ester group of both DMC and DMC reacted with lignin (Figure 3).
- The band at 1030 cm^{-1} is clearly reduced in intensity when comparing Figures 2 and 3. This peak belongs to the aromatic C-H vibration in plane, but also to the C-O in primary alcohols. Thus, its reduction could be due to the decrease

in the proportion of primary alcohols, as these have reacted with DMC.

- The bands at 1745, 1451 and 1274 cm^{-1} are practically the same and have a similar trend to the peaks found in the DMC spectrum.

Then, there are several clear trends noticeable when comparing the samples prepared at 103 °C and 180 °C (Figures. 4 and 5). While the spectra at 103 °C show well-defined peaks, the spectra of the samples at 180 °C show broad bands. This trend at 180 °C is due to two reasons: the higher degree of polymerization and crosslinking of the samples at 180 °C which causes a marked broadening of the bands, possibly indicating some thermal degradation of the material.

The peaks at 3334, 1686, and 1532 cm^{-1} are guide values of the presence of urethane bonds in the samples prepared by the three methods used [16, 21]. These peaks are very marked in all three types of preparation of samples and are absent in the spectrum of unreacted lignin.

Conversely, in the reaction between lignin and diamines, without DMC, two peaks (between 3380 and 3290 cm^{-1}) belonging to N-H stretching are observed, typically of primary amines [19, 22]. In the spectra analyzed here, only one peak is found (3334 cm^{-1}) corresponding to N-H stretching (Figure 4). This means that most of the amines present in these samples are

secondary amines, thus showing that there was reaction with the amine to form a urethane bond.

The C=O bond in amides appears at lower wavelength than in ester bonds. This explains that the value of C=O in the spectrum of LDH at 103 °C has been displaced to 1686 cm^{-1} (from 1780 cm^{-1}) due to the reaction between the DMC and HMDA. However, there are two bands in the spectrum of LDH at 180 °C within the C=O range (1763 and 1636 cm^{-1}) (Figure 5). This could mean that the amount of reacted amine with DMC is lower at 180 °C than at 103 °C. It can be interpreted as the new species formed give their peak at 1636 cm^{-1}, while the peak at 1763 cm^{-1} belongs to the remaining esters from DMC. This could be because in the case of the reaction being conducted at 180 °C, the temperature used is higher than the boiling point of HMDA, leading to its evaporation before its reaction with either DMC or lignin, or both. Conversely, Radice *et al.* [23] found that the band around 1690 cm^{-1} belongs to the carbonyl stretching vibration in associated urethane bonds.

The peak around 1530 cm^{-1} belongs to C=O and N-H deformation in the amide groups of urethane bonds but it also should be influenced by the aromatic skeleton of the lignin. The peak around 1460 cm^{-1} corresponds to the CH$_2$ scissoring and CH$_3$ deformations.

The peaks at 1300 cm^{-1} and lower are difficult to assign to one definite bond movement as they involve cooperative motions such as C-C stretching or C-O-C
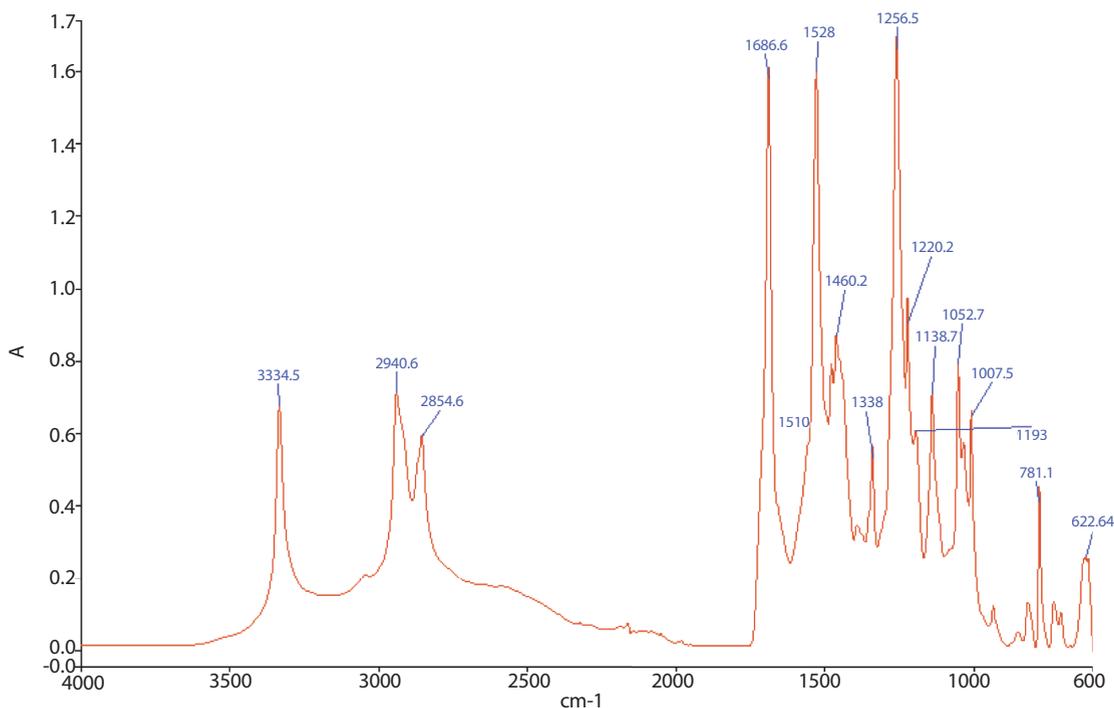
Figure 4 FTIR of the reaction LDH of lignin with dimethyl carbonate and hexamethylene diamine according to preparation method 1 at 103 °C.
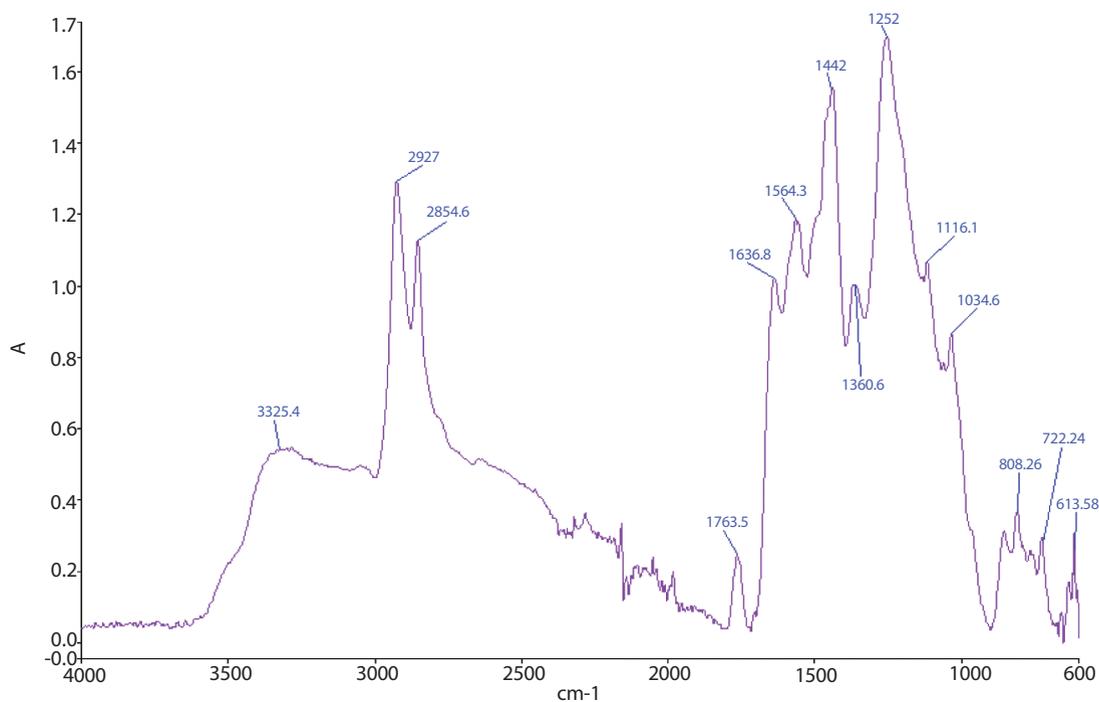
Figure 5 FTIR of the reaction LDH of lignin with dimethyl carbonate and hexamethylene diamine according to preparation method 1 at 180 °C
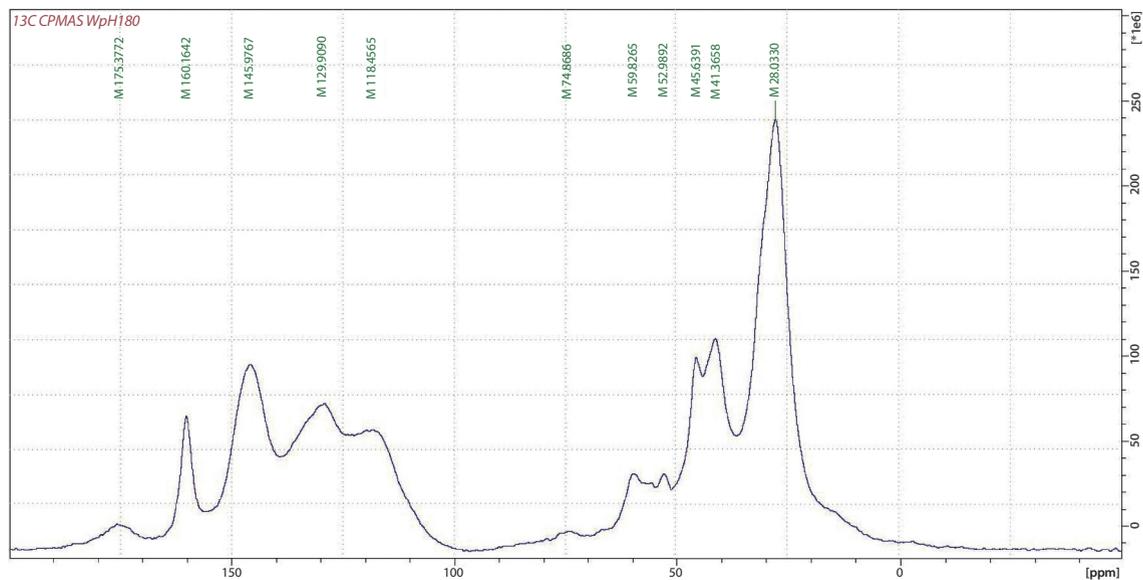
Figure 6 ^{13}C NMR spectrum of LHDWpH at 180 °C.

antisymmetric stretching. Within this range it is worth taking note of the peak at 1265–1256 cm^{-1}, which should be influenced by several bond movements, especially from the C-O stretching from the different reagents, from the lignin and from the ester group from the reaction with DMC, but also from C-N elongation.

3.3 ^{13}C NMR

Figure 6 shows the ^{13}C NMR spectrum of the sample LHDWpH at 180 °C; the spectra for the other samples and for the unreacted lignin are in the Supplementary Data. Looking at the spectrum of the sample LHDWpH

Figure 7 (Left) Sample left to harden at ambient temperature. (Right) Sample of LHDWpH after heated at 180 °C during one hour covered with a silicone sheet.

and a spectrum of the unreacted lignin, several differences can be noticed. The peaks at 75 and 86 ppm, indicating the aliphatic chain of the lignin, have practically disappeared for all the products obtained by the different methods. Also, the peak at 145–147 ppm (carbon in the aromatic ring of lignin linked with the hydroxyl group) is decreased but still present in the samples' spectra. These facts indicate that both the aromatic and the aliphatic hydroxyl groups of the lignin fragments do react to form covalent or ionic bonds. In addition, the shift at 37 ppm belonging to the C in β has disappeared, also indicating that there is reaction with the lignin. Nevertheless, their presence (145 ppm and 74 ppm) in the spectra of the obtained products seems to indicate that the reaction may not be complete.

Conversely, the unreacted DMC should show two peaks, at 156 ppm for the ester carbon and at 54 ppm for the carbon in the methyl groups. The complete absence of the first one (156 ppm) is one evidence that the DMC reacted to form a urethane bond with the HMDA or to react with the lignin. The samples also show a shift at 59 ppm, which can be attributed to the variation in the resonance of the residual methyl groups in reacted DMC. Conversely, the unreacted aliphatic HMDA should present a peak at 42 ppm. The spectra show peaks at 40–41 ppm, which suggests that there is still unreacted HMDA.

Finally, the shift at 27 ppm belongs to diamine linked either covalently or as totally ionized salts to the lignin. This shift shows a different resonance depending on the method used to prepare the samples, being 27 ppm for LDH and 28 ppm for the other two methods.

Table 4. Contact angle results obtained from the coating experiences.

Coating samples	Contact angle with wate (º)
Untreated wood	34°
LHDWpH formulation	96°
LHDpH formulation	78°
LDH formulation	88°

3.4 Contact Angle

The product obtained from the reaction of the lignin with both dymethylcarbonate and hexamethylenediamine has been applied on the surface of beech wood. When this product has been used as formed and left to harden at ambient temperature (20 °C), the hardening of the samples was not complete. However, when pressure was applied, as described in the experimental section, a homogeneous hard film was obtained on the wood surface (Figure 7). Table 4 shows the results obtained in the contact angle test. The clear increase of the values of the contact angle when compared to that of uncoated wood indicates that the application of these lignin-based coatings is effective because they increase the hydrophobicity of the wood.

4 CONCLUSIONS

- The work presented demonstrated that non-isocyanate-based polyurethanes can be prepared using kraft lignin.

- A larger number of species were observed with respect to previous works done with tannins.
- The reaction of the lignin with the hexamethylenediamine allowed the obtainment of molecules of polyurethane in which there are ionic bonds, covalent bonds or both.
- The reaction was more complete at 180 °C than at 103 °C, but a certain degree of degradation of the samples was already observed due to the high temperature, as indicated in the FTIR spectrum.

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