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 hexamethylene diamine 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 hexamethylene diamine technical grade 70% (HMDA) from Aldrich Chemical Co. Inc. (Milwaukee, USA).
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 ¹³C NMR

Solid-state CP-MAS (cross-polarization/magic angle spinning) ¹³C 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 (Krus 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), LHDWPpH 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 dimethyl carbonate to form a urethane group between the latter and the diamine. This is shown by the peak at 361 Da from the LHDWPpH spectrum at 180 °C, as follows:

$$\text{HO} \quad \text{Na}^+ \quad \text{NH} \quad \text{NH} \quad \text{O} \quad \text{O} \quad \text{CH}_3$$

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 LHDWPpH at 103 °C, as follows:

$$\text{HO} \quad \text{H}_3\text{N}^+ \quad \text{CH}_3$$

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.

$$\text{HO} \quad \text{H}_3\text{C}$$

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.

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 dimethyl carbonate (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                  |
| 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                  |
| 465,7                 | HMDA-U-DMC-182Lig-DMC-U-HMDA                      | 466                  |
| 479,7                 | HMDA-U-DMC-198Lig-DMC+Na                          | 479                  |
| 493,8                 | 305Lig-DMC-U-HMDA+Na                              | 493                  |
| 537,4                 | 154Lig-DMC-154Lig-DMC-154Lig+Na                   | 537                  |
| 538,3                 | DMC-198Lig-DMC-198Lig-DMC                         | 538                  |
| 543,6                 | 154Lig-DMC-U-HMDA-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-DMC-182Lig+Na                   | 555                  |
| 154Lig-DMC-138Lig-DMC-154Lig-DMC |                              | 556                  |
| 573,4                 | 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-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-U-HMDA+Na |                              | 713                  |
| 272Lig-DMC-U-HMDA-U-DMC-272Lig |                              | 712                  |
| 735,3                 | 138Lig-DMC-179Lig-DMC-U-HMDA+Na2                   | 736                  |
| 763,5                 | HMDA-U-DMC-138Lig-DMC-138Lig-DMC-U-HMDA+Na2       | 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 hexamethylene diamine 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                  |
| 335                   | 138Lig+-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                  |
| 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                             |                      |
| 444                   | 182Lig-HMDA-182Lig                 |                      |
| 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-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-U-DMC-180Lig-HMDA               | 712                  |
| 735,2                 | HMDA+-180Lig-HMDA-U-DMC-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                  |
| 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+Na                            | 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                  |
| 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                  |
| 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-DMC+154Lig+Na                 | 537                  |
|                       | 138Lig-HMDA-U-DMC-U-DMC+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-DMC-242Lig                    | 602                  |
|                       | 178Lig-HMDA-U-DMC-U-DMC-180Lig+Na                 | 603                  |
| 607,8                 | HMDA+-272+-HMDA-U-DMC+Na                          | 608                  |
| 613,9                 | 180Lig-HMDA-180Lig-O-+HMDA-U-DMC                   | 614                  |
|                       | HMDA+-104Lig+-HMDA+-104Lig+HMDA-U-DMC             | 614                  |
|                       | 180Lig-HMDA-180Lig-U-DMC                          | 614                  |
| 621,8                 | 178Lig-HMDA-U-DMC-U-DMC-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-DMC-242Lig                    | 642                  |
| 647,8                 | 272Lig-HMDA-U-DMC-U-DMC-154Lig                    | 648                  |
| 704                   | DMC-U-HMDA+-138Lig-HMDA-138Lig-+HMDA-U-DMC        | 704                  |
| 727,7                 | DMC-U-HMDA+-138Lig-HMDA-138Lig-U-DMC+Na           | 727                  |
|                       | DMC-U-HMDA-156Lig-HMDA-156Lig-HMDA-U-DMC+Na       | 727                  |
|                       | DMC-U-HMDA-156Lig-HMDA-138Lig-U-DMC+Na            | 727                  |
| 735                   | HMDA-180Lig-HMDA-180Lig-HMDA-U-DMC+Na             | 735                  |
| 741                   | DMC-U-HMDA-138Lig-HMDA-138Lig-HMDA-U-DMC+Na       | 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-U-DMC-198Lig                  | 790                  |
|                       | HMDA-180Lig-U-DMC-U-DMC-180Lig+HMDA-U-DMC+Na      | 789                  |
|                       | HMDA-198Lig-U-DMC-U-DMC-198Lig+HMDA-U-DMC+Na      | 789                  |
|                       | HMDA-198Lig+HMDA-180Lig+HMDA-U-DMC+Na             | 789                  |
|                       | 272Lig-HMDA-U-DMC-U-DMC-272Lig+Na                 | 789                  |
|                       | 326Lig-HMDA-U-DMC-U-DMC-326Lig                    | 790                  |
| 829,7                 | DMC-U-HMDA-+180Lig-HMDA-U-DMC+Na                  | 829                  |
|                       | DMC-U-HMDA-198Lig-HMDA-198Lig+HMDA-U-DMC+Na       | 829                  |
|                       | DMC-U-HMDA-198Lig-HMDA-198Lig-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
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.
• 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.
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
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.

### 3.4 Contact Angle

The product obtained from the reaction of the lignin with both dimethylcarbonate 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.

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

| Coating samples              | Contact angle with water (°) |
|------------------------------|------------------------------|
| Untreated wood               | 34°                          |
| LHDWpH formulation           | 96°                          |
| LHDpH formulation            | 78°                          |
| LDH formulation              | 88°                          |

### 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 hexamethylene diamine 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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