

## A new approach to improving the stability and durability of the wood

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### Abstract

The wood used in Moroccan craftsmanship has a problem of durability and dimensional stability, impregnation and polymerization of polyurethanes is an interesting way to solve both problems. However, toxic compounds based on petrochemical industries available on the market and which meet the conditions of soft wood impregnation are limited. Therefore we propose here a polyurethane synthesis pathway based on the reaction of diamines with dicarbonates, the dicarbonates are obtained here by additions of two glycerol carbonate groups on a connecting link. The treatments were carried out in two steps involving first impregnation of dicarbonate in acetone, followed by a second with diamine dissolved in dichloromethane or in water depending on its solubility. The effect of the treatment was evaluated with and without leaching the wood by measuring its dimensional stability and sustainability against *Poria placenta*. Results were promising with ASE values, 70% ASE for an approximately weight gain of 30% after leaching. Biological tests also indicated an improvement in the durability of the wood to rot.

## 1. Introduction

Dimensional stabilization and sustainability are two crucial points for the use of wood in most Moroccan craft applications. Indeed, the timber is a very hygroscopic material, whose dimensions vary considerably depending on the ambient humidity. One way to avoid the dimensional variations of the timber is to impregnate it with water-soluble compounds such as polyethylene glycols or polyglycerol able to interact with the biopolymers of the wood cell walls limiting the phenomena of shrinkage during drying, such modifications possible not only to impart to the greater dimensional stability of the material, but also, according to the performed modification, increase its resistance to biodegradation of agents such as decay fungi with non biocidal new alternatives to the use of certain products of toxic preservatives.

The most important development of the diester as a green fuel to reduce emissions of greenhouse gases, leading to the formation of significant amounts of glycerol why it is necessary to find applications. In this context, we specifically explore the uses of glycerol carbonate and its derivatives to develop new wood treatment products. We have proposed new approaches based on hydroxypolyurethanes [1-6], obtained from very affordable starting compounds by a dead isocyanate: from works of literature [7-15] Two different approaches were considered for this purpose:

- The first concerns the direct use of glycerol carbonate to develop treatments followed by aqueous phase, after impregnation of the product in the woods, a polymerization reaction for attaching it to prevent leaching.
- The second involves the formation of polyurethanes in the timber without requiring the use of isocyanates from glycerol carbonate dicarbonates (CG) and diamines.

## 2. Experimental details

### 2.1. Apparatus

#### 2.1.1. RMN et FTIR

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in water on a Bruker DRX 400 spectrometer. Chemical shifts are expressed in parts permillion. FTIR spectra were recorded as thin films between NaCl plates on a Perkin Elmer FTIR spectrometer SPECTRUM 2000.

#### 2.1.2. Thermogravimetric Analysis

TG / DTA analyzes were performed on a TG-DTG apparatus 92 (Setaram). This device is coupled to a mass spectrometer to analyze volatile products formed during the degradation of the compounds analyzed. Ionization of these volatiles is by electron impact. Analytical crucibles are alumina and the mass of sample required is about 60 mg.

#### 2.1.3. Size exclusion chromatography analysis (GPC)

The degree of polymerization of the polymers was determined using a size exclusion chromatographic analysis (GPC). The column used was the Phenogel column ball 5  $\mu\text{m}$ , which is the maximum precision for molar masses between 500 and 6000 g / mol; the pore diameter is 10 nm and the detection is performed by a refractometer. The volume of the injection loop was 20  $\mu\text{l}$  and the eluting solvent is DMF. Before use, the column was calibrated using polyethylene glycol standards 6 molar mass ( $M_w$ ) determined: 200, 400, 600, 1000, 3000 and 6000 g / mol. The calibration of the method enabled to increase log ( $M_w$ ) based on retention time and to determine the linear area. Here it is between five and ten minutes of retention in the column. Outside these limits, the molar masses are no longer significant.

### 2.2. Impregnation procedure

Beech (*Fagus sylvatica*) heartwood was used for this study. Blocks of 15×5×25 mm in radial, tangential and longitudinal directions respectively were dried at 50°C for 48 h and weighed ( $m_0$ ). Dried blocks (70 replicates) were placed in a 500 mL beaker inside a dessicator equipped with a two-way tap and subjected to a 5 mbar vacuum for 20 min. Blocks were then impregnated by suction with reagents solutions. The weight gain observed after drying was expressed according to the following formula.

$$\text{WG (\%)} = ((m_1 - m_0) / (m_0)) \times 100$$

Where  $m_0$  is the initial dried mass and  $m_1$  is the impregnated dried mass.

### 2.3. Leaching test tubes

Fixing the product in the timber after polymerization was evaluated in two ways, either by performing leaching Soxhlet or by making different periods of leaching in a simplified procedure inspired by the NF X41-565. Each specimen is placed in a container with five times its volume of distilled water, which itself is placed on a mechanical shaker. They are then subjected to a first phase of maceration realizing three leaching cycles (1, 2, 4 hours) with change of the water between each cycle. The specimens are then dried and weighed ( $m_2$ ). The percentage of leached product is determined by the following formula:

$$\text{Percentage of leached product (\%)} = ((m_1 - m_2) / (m_1 - m_0)) \times 100$$

Where  $m_0$  is the dry mass of the untreated sample,  $m_1$  the dry mass of the specimen processed before leaching  $m_2$  and its anhydrous mass after leaching.

### 2.4. Measurement of anti-swelling efficiency

The influence of treatment on dimensional stability is assessed by measuring the ASE (Anti Swelling Efficiency). This value expressed as a percentage, the reduction of swelling (or removal) of wood treated compared to untreated wood. The calculation of the ESA is from swelling coefficients according to the following equations:

$$S (\%) = ((V_h - V_s) / V_s) \times 100$$

where S is the swelling coefficient,  $V_h$  the volume of wet wood and  $V_s$  the volume of dry wood.

$$ASE (\%) = ((S_0 - S_1) / S_0) \times 100$$

where  $S_0$  is the swelling coefficient of untreated wood and  $S_1$  the treated wood.

## 2.5. Treatment of specimens by dicarbonates / diamine in two stages

The specimens of beech (*Fagus sylvatica*) are prepared by a protocol similar to that recommended by the European Standard EN113. With initial dimensions of 1.5x2.5x5cm according to the radial directions, tangential and longitudinal, are previously dried in an oven (70°C for two days) and then treated successively with dicarbonates solutions and aqueous (or organic if necessary) of the diamine as described below:

A dicarbonate solution is vacuum impregnated in 50 ml of aqueous (or organic if necessary), the specimens were dried at 70°C for two days before being impregnated with new one equivalent of diamine in 50 ml of water or suitable organic solvent.

## 2.6. Bioassays

Bioassays were carried out on beech samples exposed to the action of *Poria placenta*-rot fungus responsible for 70% of the damage listed in indoors. Other tests with *Coriolus versicolor* could not be operated due to significant contamination of the culture medium.

40 g of malt and 30 g of agar are dissolved in one liter of distilled water. The mixture is homogenized by heating the solution at 50°C. The pH of the mixture was adjusted to 4.8 with a hydrochloric acid solution (0.5N). The mixture was then sterilized by autoclaving at 120°C for 25 minutes. After cooling, the still warm sterilized mixture (about 40 °C) is poured at a rate of about 20 ml in the Petri dishes of 8.5 cm in diameter under a laminar flow hood near a flame. The cans are then left one hour under the hood so as to allow the medium to solidify.

Under sterile conditions (laminar flow hood and near a flame), the plates were inoculated with a piece of mycelium of a freshly transplanted culture of *Poria placenta* introduced in the middle of agar medium. The Petri dishes are placed in a climatic chamber Binder KBF 115 brand regulated at 22°C and 70% RH, and left for a week in order to permit the colonization of the entire surface of the box by the mycelium.

Treated or not pre-dried test specimens at 100°C are then placed in contact with the fungus under sterile conditions and the petri dishes are closed with parafilm. These are allowed to incubate for 16 weeks in a climatic chamber at 22°C and 70% H A. Each test is performed twice with four samples per plate (3 treated and one untreated).

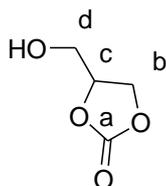
At the end of the incubation period, the samples are removed from the Petri dishes, freed from mycelium and weighed ( $m_1$ ). The specimens were then dried at 55°C for 48 hours and weighed ( $m_2$ ). The sample mass loss is then determined by the formula below.

$$\text{Mass loss (\%)} = [(m_0 - m_2) / m_0] \times 100$$

## 2.7. Products

### 2.7.1. Glycerol Carbonate

Crude glycerol carbonate is purified by distillation under reduced pressure in a suitable mounting. After removing the top fraction, glycerol carbonate is recovered as a viscous colorless liquid with a temperature level of 152 °C to a pressure of 5 mbar.

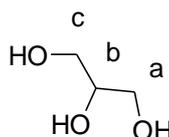


**FTIR<sub>vC=O</sub> (NaCl film):** 3401 cm<sup>-1</sup> (wide, OH); 2931 cm<sup>-1</sup> (C-H aliphatic); 1780 cm<sup>-1</sup> (C=O cyclic carbonate).

**RMN<sup>1</sup>H (DMSO d<sub>6</sub>):** δ = 3,52 ppm (dd, J<sub>1</sub> = 16,6 Hz, J<sub>2</sub> = 3,1 Hz, 2H, d); δ = 4,42 ppm (dd, J<sub>1</sub> = 21,1 Hz, J<sub>2</sub> = 1,5 Hz, 2H, b); δ = 4,81-4,76 ppm (m, 1H, c); δ = 5,23 ppm (s, 1H, OH).

**RMN<sup>13</sup>C (DMSO d<sub>6</sub>):** δ = 155,4 ppm (a); δ = 77,1 ppm (c); δ = 65,9 ppm (d); δ = 60,9 ppm (b).

## 2.6.2. Glycérol



**FTIR**<sub>vC=O</sub> (NaCl film): 3403 cm<sup>-1</sup> (wide, OH); 2942 cm<sup>-1</sup> (C-H aliphatic).

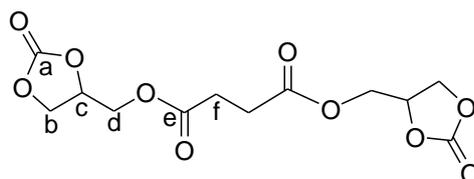
**RMN**<sup>1H</sup> (DMSO d<sub>6</sub>): δ = 3, 27-3, 43 ppm (m, 5H, a,b,c); δ = 4,41 ppm (s, 3H, OH).

**RMN**<sup>13C</sup> (DMSO d<sub>6</sub>): δ = 70, 2 ppm (b); δ = 62, 7 ppm (a, c).

## 2.8. General procedure for esterification with diacid chlorides

In a 100 ml two-necked reactor equipped with a condenser and an addition funnel were placed 2 equivalents (4 g, 33 mmol) of glycerol carbonate diluted in 10 ml of dichloromethane with 2 equivalents (33 mmol, 2.6 g) of pyridine or triethylamine. The mixture is cooled to 0°C using an ice bath. 1 equivalent of diacid chloride diluted in 10 ml of dichloromethane is added dropwise to the reaction mixture. After addition, the ice bath was removed and the mixture allowed warming to room temperature. After 4 h stirring at room temperature, the reaction mixture is poured into a separatory funnel and treated with water. The organic phase is separated, washed successively with a solution (2x50 ml) of hydrochloric acid (1M), a chilled solution (2x50 ml) of sodium bicarbonate at 5%, then with water before being dried on magnesium sulfate. The solvent was evaporated in vacuo and the product obtained characterized by NMR and FTIR.

- Product **1**

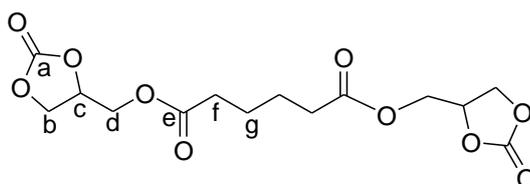


**FTIR**<sub>vC=O</sub>(NaCl film): 2967 cm<sup>-1</sup> (C-H aliphatic); 1781 cm<sup>-1</sup> (C=O cyclic carbonate); 1741 cm<sup>-1</sup> (C=O ester).

**RMN**<sup>1H</sup> (DMSO d<sub>6</sub>): δ = 5,06 ppm (s, 1H, c); δ = 4,35-4,57 ppm (m, 6H, b, d); δ = 4,05-4,32 ppm (m, 2H, a); δ = 2,60- 2,64 ppm (m, 4H, f).

**RMN**<sup>13C</sup> (DMSO d<sub>6</sub>): δ = 172,0 ppm (e); δ = 155,1 ppm (a); δ = 74,4 ppm (c); δ = 66,4 ppm (d); δ = 63,7 ppm (b); δ = 28,8 ppm (f).

- Product **2** and **3**



**FTIR**<sub>vC=O</sub>(NaCl film): 2977 cm<sup>-1</sup> (C-H aliphatic); 1801 cm<sup>-1</sup> (C=O cyclic carbonate); 1734 cm<sup>-1</sup> (C=O ester).

**RMN**<sup>1H</sup> (DMSO d<sub>6</sub>): δ = 5,04 ppm (s, 1H, c); δ = 4,52-4,58 ppm (m, 6H, b, d); δ = 4,10-4,33 ppm (m, 2H, a); δ = 2,52- 2,63 ppm (m, 4H, f); δ = 1,53- 1,60 ppm (m, 4H, g);

**RMN**<sup>13C</sup> (DMSO d<sub>6</sub>): δ = 172,6 ppm (e); δ = 155,0 ppm (a); δ = 74,6 ppm (c); δ = 66,3 ppm (d); δ = 60,0 ppm (b); δ = 33,2 ppm (f), δ = 23,0 ppm (g).

## 3. Results and Discussion

### 3.1. Direct polymerization of glycerol carbonate

Two strategies involving in situ polymerization of glycerol carbonate in the wood after impregnation were considered: A first possibility relates to the formation of a polycarbonate in the timber resulting from self-condensation reaction of glycerol carbonate on itself same may or may not be related to the wood. The second possibility concerns the polyglycerol training in the woods following a first decarboxylation reaction glycerol carbonate leading to glycidol capable of polymerizing into the wood to lead to the formation of polyglycerol.

The thermal stability of glycerol carbonate and its decarboxylation temperature and chemical reactivity have been studied. The analysis was carried out in air for a range of temperatures between 20 and 500°C with a temperature rise of 5°/min (Figure 1).

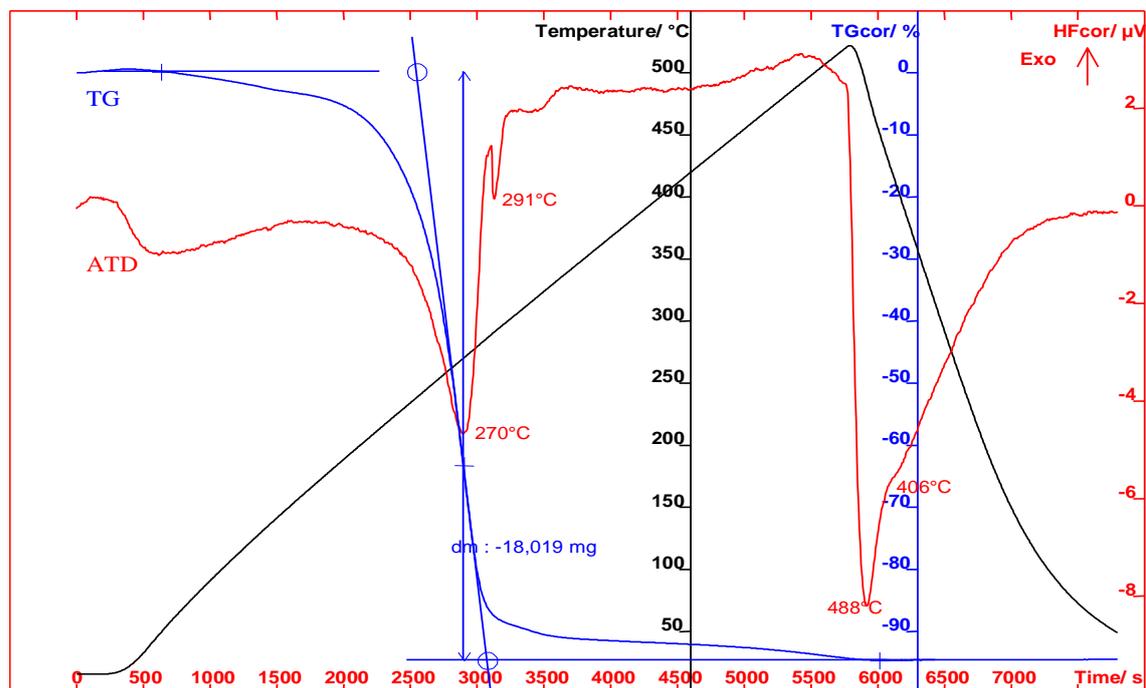


Figure 1: Analysis TG / DTA glycerol carbonate

The figure shows two curves:

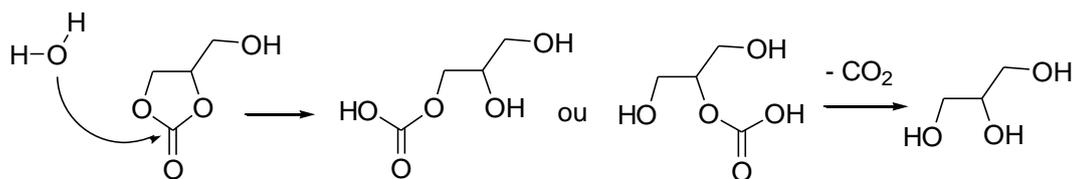
- TG: thermogravimetric curve (weight loss)
- ATD: differential thermal curve

Thermogravimetric analysis indicated that the weight loss is relatively low up to about 200-220°C temperatures. It appears that the product is not decarboxylated below 220°C. Small weight losses observed below this temperature are due to the presence of water in the starting material. Beyond these temperatures, there is a rapid increase in the weight loss that is almost complete at 300°C. The differential analysis indicates an exotherm to 270°C corresponding to the product of the decarboxylation to give glycidol which vaporizes quickly leading to a substantially complete mass loss.

Following these results, it appears that the channel B involving polyglycerol in situ formation in wood by the decarboxylation of glycerol carbonate requires too high a temperature to consider the formation of a wood-polymer composite directly without degrading the constituents of wood. The latter is known to begin to deteriorate in a temperature range between 200 and 300°C [16].

The other possibility to polymerize glycerol carbonate is to consider the formation of a polycarbonate. This polycondensation reaction involves the opening of the carbonate ring with a hydroxyl group which may belong to the carbonate of glycerol or from another molecule. Moreover, this different sites glycerol carbonate electrophiles capable of reacting with nucleophiles [17,18, 19] as the hydroxyl groups present on the polymers constituting the timber such as cellulose, hemicellulose or lignin.

The various tests carried out have shown that alcohols hardly reacted with glycerol carbonate at temperatures below 140°C. Higher temperatures lead to its glycerol hydrolysis. The formation of the latter results from the presence of water in the starting material, the quantity was estimated at 2.5% following steps using a thermobalance. Water would be capable of hydrolyzing glycerol carbonate resulting in the formation of carboxylic acids which spontaneously decarboxylate to give glycerol (Figure 2).



**Figure 2:** Hydrolysis of glycerol Training

Given the difficulties encountered in situ polymerizing glycerol carbonate directly into the wood, we turned to a different approach with the use of polyurethanes.

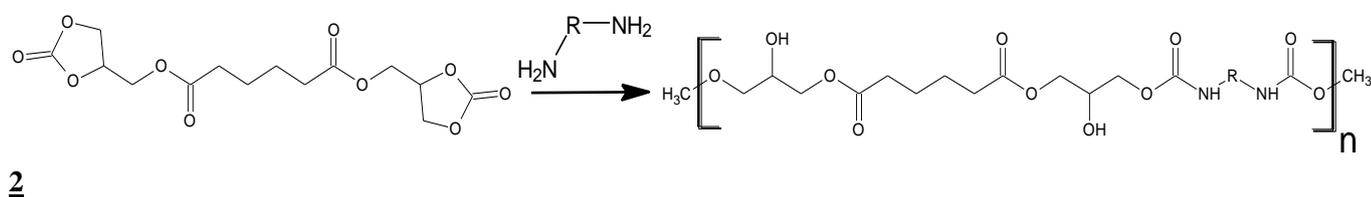
### 3.2. Using polyurethane

The high reactivity of the cyclic carbonate compared to carbonate functional primary amines, led us to consider the formation of dicarbonates for the synthesis of polyurethanes. The use of one equivalent of glycerol carbonate with 0.5 equivalent of the diacid chloride as connecting link leads to the expected dicarbonates with good yields. The results obtained are reported in Table 1.

**Table 1:** Synthesis of dicarbonates from glycerol carbonate (1eq) and the diacid chloride (0.5eq).

Product	Operating Conditions	R	Yield (%)
<u>1</u>	triethylamine (1 éq), CH <sub>2</sub> Cl <sub>2</sub> , 4 h, 25°C	-CH <sub>2</sub> -CH <sub>2</sub> -	54
<u>2</u>	triethylamine (1 éq), CH <sub>2</sub> Cl <sub>2</sub> , 4 h, 25°C	-CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>2</sub> -	77
<u>3</u>	pyridine (1 éq), CH <sub>2</sub> Cl <sub>2</sub> , 4 h, 25°C	-CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>2</sub> -	67

In view of these results, the dicarbonates formation using a diacid chloride and glycerol carbonate appears as a simple and easy to implement. In addition, it enables full control of the final product structure, which can be a significant advantage when implementing subsequent polycondensation reactions. We then studied the formation of polyurethanes from dicarbonate 2 by reacting the latter with diamines (Figure 3).



**Figure 3:** Formation of polyurethane

Table 2 shows the results obtained using different operating conditions, the progress of the reaction is characterized by IR spectroscopy we always based on the signals at 1780 cm<sup>-1</sup>, characteristic of the carbonyl of the cyclic carbonate and 1704 cm<sup>-1</sup> characteristic carbamate.

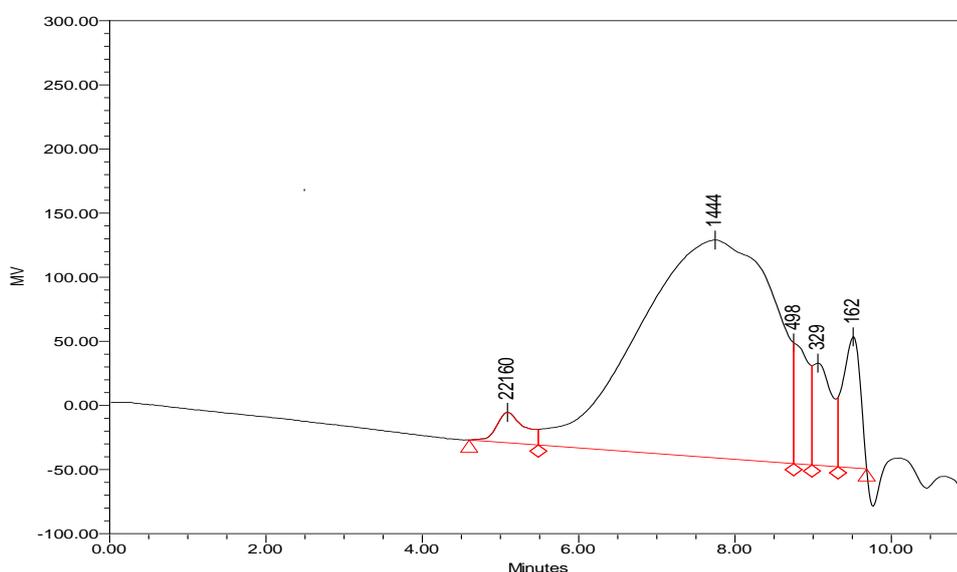
The IR analysis performed indicates the disappearance of the characteristic band of the carbonyl of the cyclic carbonate ground to 1780 cm<sup>-1</sup> and the appearance of a new band at around 1704 cm<sup>-1</sup> characteristic of the formation of carbamate links polyurethane. <sup>1</sup>H NMR analysis of the different reaction products shown in all cases disappearance of the characteristic signal pattern of the cyclic carbonate.

**Table 2:** Reactivity dicarbonate **2** (1eq) with various diamines (1eq)

Reaction Conditions	$\nu_{C=O}$ à 1780 $\text{cm}^{-1}$	$\nu_{C=O}$ à 1704 $\text{cm}^{-1}$
Ethylènediamine, 10 ml $\text{CH}_2\text{Cl}_2$ , 60°C, 1 h	Disappearance	Appearance
Butylènediamine, 10 ml $\text{CH}_2\text{Cl}_2$ , 60°C, 1 h	Disappearance	Appearance
Hexanediamine, 10 ml $\text{CH}_2\text{Cl}_2$ , 60°C, 1 h	Disappearance	Appearance
Diéthylènetriamine, 10 ml $\text{CH}_2\text{Cl}_2$ , 60°C, 1 h	Disappearance	Appearance

Various diamines such as ethylenediamine, butylenediamine, hexanediamine, lysine monohydrate, a triamine: tetramine and diethylenetriamine: tris (2-aminoethyl) amine were considered to form the polyurethane. The major difference between these different amines regards their solubility in water or not.

The progress of the reaction characterized by IR spectroscopy are always based on the signals at 1780  $\text{cm}^{-1}$ , characteristic carbonyl of cyclic carbonate and 1704  $\text{cm}^{-1}$  characteristic of carbamate. The efficiency of the reaction was assessed by NMR spectroscopy and by size exclusion chromatography SEC (Figure 4).

**Figure 4:** polyurethane size exclusion chromatogram obtained with butylenediamine

Treatments were used to treat wood in two steps involving first impregnation dicarbonate in acetone, followed by a second with the diamine dissolved in dichloromethane or in water depending on its solubility. The effect of treatment on the wood was evaluated with and without leaching by measuring its dimensional stability and comparing to sustainability *Poria placenta*. The results obtained are reported in Table 3.

According to the impregnation solutions used, the mass gains are around 30% dicarbonate system / hexanediamine and 35% for dicarbonate system / diethylenetriamine. This difference is explained by the solubility dicarbonate and nature of the solvent used to impregnate it into the woods. Dicarbonate **2** insoluble in water is impregnated in acetone does not allow such a significant penetration into the cell walls. The effect on the dimensional stability is less of it is marked. Again, it is observed after leaching decreased more or less significant weight gain as a function of the nature of the solvent and leaching method used. However, it is noted that an important part of the product remains in the impregnated wood, the resulting polyurethane formation which has improved resistance to leaching. The results obtained with the leaching to water, especially those made with cold water are very encouraging as they show that the polyurethane is only weakly leached under conditions of outdoor uses. The polymerization of the product in the wood has also been studied by IR analysis of samples after treatment (Figure 5).

**Table 3:** Impregnation tests with dicarbonate **2** and various diamines

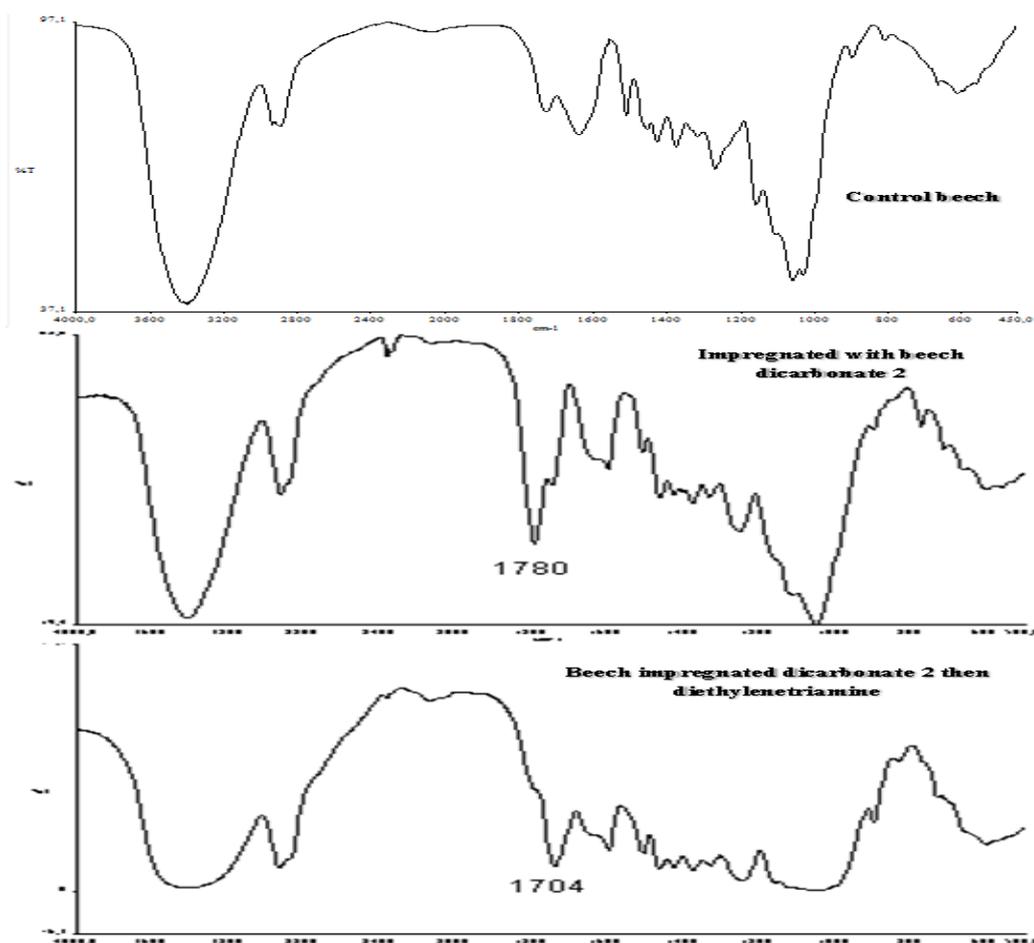
Treatment	Impregnating solution	Leaching	Before leaching		After leaching		Leached product(%)
			Weight gain (%)	ASE (%)	Weight gain (%)	ASE (%)	
A	Dicarbonate <b>2</b> (10 g) in acetone (50 mL), and hexanediamine (3.35 g) in CH <sub>2</sub> Cl <sub>2</sub> (50 ml)	Water <sup>a</sup>	28,6	18,6	9,7	4,8	65,8
		Acétone <sup>b</sup>	28,5	17,8	13,2	5,5	53,6
		CH <sub>2</sub> Cl <sub>2</sub> <sup>c</sup>	29,6	23,5	20,5	20,6	30,8
		Water <sup>d</sup>	31,8	22,3	25,8	18,2	18,9
B	Dicarbonate <b>2</b> (10,5 g) in acetone (50 ml), and diéthylènetriamine (3,12 g) in water (50 ml)	Water <sup>a</sup>	30,6	27,4	18,2	9,3	40,6
		Acétone <sup>b</sup>	34,4	28,8	24,6	11,5	28,5
		CH <sub>2</sub> Cl <sub>2</sub> <sup>c</sup>	36,6	33,2	32,1	31,7	12,3
		Water <sup>d</sup>	35,2	30,1	28,7	25,2	18,4

(a) Soxhlet leaching to water for 6 h, average of 6 samples

(b) Leaching soxhlet with acetone for 6 h, average of 6 samples

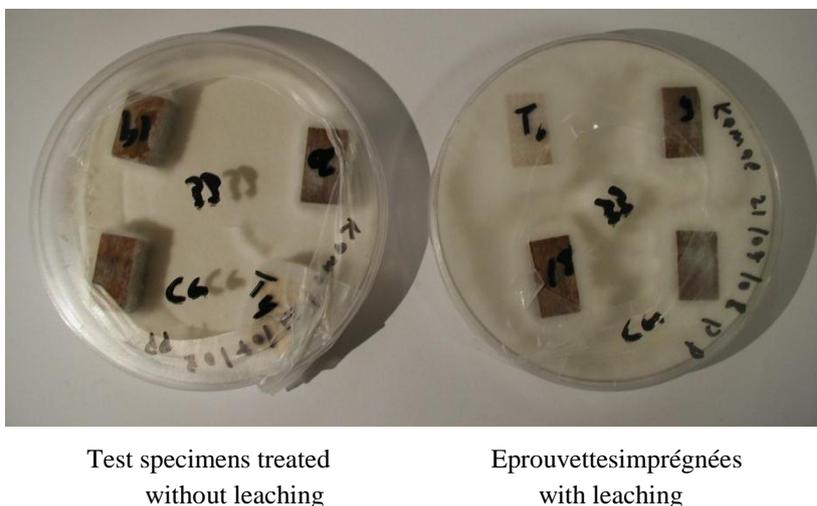
(c) Soxhlet leaching, dichloromethane for 6 h, average of 6 samples

(d) Leaching in cold water with water change after 1 h, 2 h, 4 h, 12 h, average of 6 samples

**Figure 5:** FTIR spectra showing the formation of the polyurethane in the timber. Control beech, Impregnated with beech dicarbonate **2**, (each impregnated dicarbonate **2** then diethylenetriamine)

FTIR spectra of the sawdust, obtained after grinding of the samples impregnated successively dicarbonate **2** and diethylenetriamine confirm the formation of the polyurethane. The disappearance of the band at  $1780\text{ cm}^{-1}$ , characteristic carbonyl functions cyclic carbonates in favor of bands to  $1704\text{ cm}^{-1}$  characteristic of the formation of carbamate unambiguously indicates the formation of polyurethane in the wood.

The effect of treatment on the durability of the wood was evaluated with *Poria placenta*. The results are shown in Figure 6 and Table 4. The appearance of the specimens at the end of 16 weeks of exposure *Poria placenta* clearly indicates a protective effect of treatment carried out with the dicarbonate **2** and the diamine. Indeed, while the control samples are completely covered by the mycelium, the treated samples have practically not been colonized by the fungus.



**Figure 6:** Aspect specimens treated or not by the polyurethane obtained after impregnation dicarbonate **2** and diethylenetriamine after 16 weeks of exposure to *Poria placenta*

**Table 4:** Mass losses of treated samples with dicarbonate **2** and various diamines

Impregnating solution	Test tube	$m_0$ (g)	$m_1$ (g)	Weight loss(%)
Dicarbonate <b>2</b> (10 g) in acetone (50 mL), then hexanediamine (3.35 g) in $\text{CH}_2\text{Cl}_2$ (50 ml) without leaching	witness	1,16	0,95	18,14
	treated <sup>c</sup>	1,18	1,14	$3,11 \pm 0,30$
Dicarbonate <b>2</b> (10 g) in acetone (50 mL), then hexanediamine (3.35 g) in $\text{CH}_2\text{Cl}_2$ (50 ml) with leaching <sup>a</sup>	witness	1,11	0,88	20,83
	treated <sup>c</sup>	1,07	1,04	$3,15 \pm 0,18$
Dicarbonate <b>2</b> (10 g) in acetone (50 mL), then hexanediamine (3.35 g) in $\text{CH}_2\text{Cl}_2$ (50 ml) with leaching <sup>b</sup>	witness	1,13	0,89	21,23
	treated <sup>c</sup>	1,09	1,05	$3,72 \pm 0,55$
Dicarbonate <b>2</b> (10.5 g) in acetone (50 ml) and then diethylenetriamine (3.12 g) in water (50 ml) without leaching	witness	1,13	0,87	22,92
	traitée <sup>c</sup>	1,35	1,32	$2,06 \pm 0,36$
Dicarbonate <b>2</b> (10.5 g) in acetone (50 ml) and then diethylenetriamine (3.12 g) in water (50 ml) with leaching <sup>b</sup>	witness	1,15	0,79	30,86
	treated <sup>c</sup>	1,33	1,30	$2,26 \pm 0,03$

<sup>a</sup>washed with acetone soxhlet during 6 h

<sup>b</sup>washed with water soxhlet during 6 h

<sup>c</sup>average over 3 samples

The results show that the modified samples exhibit improved resistance to fungal degradation. Indeed, the treated specimens leached or not, have very low mass loss compared to control samples that are highly degraded. Visual observation of the test specimens in the end also indicates that the mycelium does not develop or very little on the treated specimens.

## Conclusion

In situ polymerization of glycerol carbonate to form either a polycarbonate or polyglycerol is not feasible under conditions suitable for the treatment of wood. Using dicarbonates resulting in polyurethane after reaction with various diamines is against much more promising. Successive impregnation into the wood of two solutions containing dicarbonate and a diamine for synthesizing polyurethane in situ can dimensionally stabilize the wood. These treatments can be carried out in organic phase or in aqueous phase according to the choice of the products used. Leaching tests show a good fixing of the product in the timber. The first confrontation test specimens treated rot fungi action as *Poria placenta*-rot fungus, allowed to show that the treated samples showed increased durability to biodegradation.

## References

1. Salman S., Petrissans A., Thevenon M-F., Dumarcay S., Perrin D., Pollier B., Gerardin P., *Eur. J. Wood Prod.* 72 (2015) 355-365.
2. Cleland M.R., Galloway R.A., Berejka A.J., Montoney D., Driscoll M., Smith L., Scott Larsen L., *Radiat. Phys. Chem.* 78 (2009) 535-538.
3. Nohra B., Candy L., Blanco J.F., Guerin C., Raoul Y., Mouloungui Z., *Macromolecules.* 46 (2013) 3771–3792.
4. Fleischer M., Blattmann H., Mülhaupt R., *Green Chem.* 15 (2013) 934.
5. Unverferth M., Kreye O., Prohammer A., Meier M.A., *Macromol. Rapid Commun.* 34 (2013) 1569-1574.
6. Bähr M., Bitto A., Mülhaupt R., *Green Chem.* 14 (2012) 1447.
7. Obounou F., Gerardin P., Thevenon M-F., Gerardin C., *Wood Sci Technol.* 49 (2015) 443.
8. Webster, D.C., *Prog. Org. Coat.* 47(2003) 77-86.
9. Ochiai, B., Satoh, Y., Endo, T., *Green Chemistry.* 7 (2005) 765-767.
10. Ubaghs, L., Fricke, N., Keul, H., Höcker, H., *Macromol. Rapid Commun.* 25 (2004) 517-521.
11. Hakkou M., Pétrissans M., Zoulalian A., Gérardin P., *Polym Degrad Stab.* 89 (2004)1-5
12. Fabbri D., Bevoni V., Notari M., Rivetti F., *Fuel-Elsevier.* 86 (2007) 690–697
13. George J., Patel, Muthukumar S. P., Munshi P., *J. Mol. Catal. A: Chem.* 304 (2009) 1–7.
14. Behr A., IrawadaJ.K., *Green Chem.* 10 (2008) 13-30.
15. Steblyanko A., Choi W., Sanda F., Endo T., *J. Polym. Sci., Part A: Polym. Chem.* 38 (2000) 2375–2380.
16. Hakkou M., Pétrissans M., Zoulalian A., Gérardin P., *Polym Degrad Stab.* 89 (2005) 1-5.
17. Stafslie S., Sommer S., Webster D., Bodkhe R., Pieper R., Daniels J., Vander Wal L., Callow M., Callow J., Ralston E., Swain G., Brewer L., Wendt D., Dickinson G., Lim C., Teo S.L., *Biofouling.*, 32 (2016) 949-968.
18. Rokicki G., Rakoczy P., Parzuchowski P., Sobiecki M., *Green Chem.* 7 (2005) 529-539.
19. Iaych K., Dumarcay S., Gérardin P., Belakhmima R., Ebn Touhami M., Chaouch M., *J. Mater. Environ. Sci.* 6 (11) (2015) 3245-3250.

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