



## Investigations on wood treatment by eco-friendly hydroxypolyurethanes

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### ABSTRACT

Dimensional stabilisation is a crucial point for using wood in most of the structural applications. Among numerous methods, impregnation and polymerization of polyurethanes is an interesting way to achieve this stabilisation. However the important amounts requirement of petrochemical and toxic compounds is a strong drawback to develop this approach on the market. Therefore we propose here an isocyanate-free route based on the reaction of various diamines with dicarbonates obtained by addition of two glycerol carbonates moieties on a linker. In a first time, the mildest conditions to perform the reaction are researched with model mono- and polyamines without wood: the solvent, temperature, number of equivalent and regioselectivity are investigated. In a second time, two steps procedures are applied to beech wood blocks. The key step is a polycondensation is performed *in situ* in beech blocks after impregnation of the monomers using a double vacuum procedure involving successively impregnation of cyclic carbonate and polyamine, respectively. Resistance of treatment to leaching and anti swelling efficiency before and after leaching have been determined. Decay durability has been also evaluated using the white rot fungus *Coriolus versicolor*. Despite some difficulties to carry out this procedure conveniently in terms of impregnation solvents and step numbers, the results are promising with ASE values of about 70% for a weight gain of approximately 30 % after leaching. Biological tests indicated also an improvement of wood durability to decay.

### INTRODUCTION

Dimensional stabilization is a crucial point for using wood in most of the structural applications. Actually, the wood polysaccharidic part is strongly hydrophilic and swelling effects occur by intake or evaporation of water molecules when temperature and hygrometry are changing. In order to avoid these phenomenon, a solution could be the filling of existing cavities and/or the withdrawing of water by hydrophilic polymers like the wide-used PEGs. However, they are sensitive to oxidation and their leachability prevents them from being used in Use Class 3 for example. Therefore we proposed new approaches based on hydroxypolyurethanes obtained from very affordable starting compounds by an isocyanate-free route: based on literature works (Rokicki and Piotrowska 2002, Webster 2003, Ochiai *et al.* 2005, Ubaghs *et al.* 2004), several ways were investigated involving either glycerol carbonate (GC) produced from a Biodiesel plant by-product or carbonated polyglycerol (DCPG3), impregnated into the wood and reacting with primary diamines.

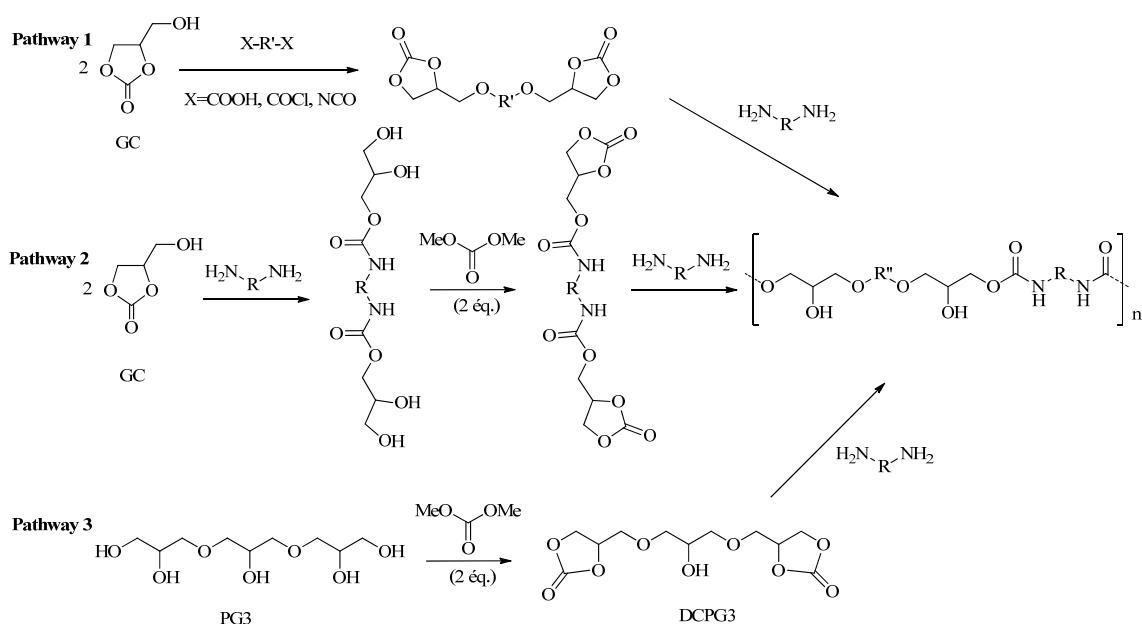


Figure 1: The 3 investigated pathways to prepare hydroxypolyurethanes

In a first time, three pathways have been investigated (Figure 1) to evaluate their compatibility with some wood use prerequisites, particularly in terms of maximal reaction temperature and also the reactivity in presence of water. Two of them were based on the use of glycerol carbonate (GC) which is a by-product of the Diester industry. Then the procedures have been applied to wood samples to check the treatments efficiency by measurement of ASE before and after leaching as well as the ability to improve wood resistance versus fungal attacks expected by the material chemical composition changes.

## EXPERIMENTAL

### Materials

Dimethyl carbonate (DMC), the solvents and the di- and tri- amines were purchased from Fluka-Sigma-Aldrich Chimie SARL (St Quentin Fallavier, France). Glycerol carbonate was obtained from Novance (Compiègne, France); Polyglycerol was also obtained from Novance as a mixture of compounds with an average molecular weight of 242 ( $n \sim 3$ ).

### Instruments

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

### Synthesis of polyglycerol carbonate (DCPG3)

In a 100 mL round bottomed flask equipped with a magnetic stirrer, a condenser and a thermometer, polyglycerol (2.10 g, 8.6 mmol), dimethyl carbonate (1.55 g, 17.2 mmol) and  $\text{K}_2\text{CO}_3$  as catalyst (60 mg, 0.43 mmol) were placed. The reaction was carried out under reflux for 5 h. Methanol and residual DMC were then evaporated under reduced pressure.

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ),  $\delta$  (ppm): 4.89 (m, 2H); 4.81-4.77 (broad s, OH); 4.51 (m, 2H); 4.28 (m, 2H); 3.78-3.16 (m, polyglycerol protons)  
 FTIR (NaCl film),  $\nu$  ( $\text{cm}^{-1}$ ): 3401, 2931, 1781, 1403, 1181, 1054

### ***Reaction of carbonates with amines, general procedure***

Five membered cyclic carbonate of polyglycerol was mixed with amine at room temperature in a round bottomed flask equipped with a magnetic stirrer. Progress of the reaction was monitored by FT-IR spectroscopy following the disappearance of the cyclic carbonyl band at  $1781\text{ cm}^{-1}$ .

### ***Impregnation procedure***

Beech (*Fagus sylvatica*) heartwood was used for this study. Blocks of 15 x 5 x 25 mm in radial, tangential and longitudinal directions respectively were dried at  $50\text{ }^\circ\text{C}$  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.

### ***Decay studies***

Decay resistance was studied using a malt agar plate decay test which is a modification of the standardised EN 113 test involving the brown-rot basidiomycete *Poria placenta*. Sterile culture medium (20 mL), prepared from malt (30 g) and agar (40 g) in distilled water (1.0 L), were placed on 9.0 cm Petri dishes, inoculated with fungus and incubated for 1 week at  $22\text{ }^\circ\text{C}$  and relative humidity (RH) of 70 % to allow colonisation of the medium by the mycelium. Three U.V. sterilized wood blocks (treated or untreated) were then placed in each Petri dish under sterile conditions. Incubation was carried out at  $22\text{ }^\circ\text{C}$  and 70 % RH for 16 weeks. The weight loss (WL) due to fungal attack was expressed according to the following formula (Eqn. 1):

$$\text{WL (\%)} = [(m_0 - m_1)/m_0] \times 100 \quad (1)$$

where  $m_0$  is the initial dried mass and  $m_1$  is the dried mass after exposure to *P. placenta*.

## **RESULTS AND DISCUSSION**

### ***First part: method development without wood***

#### Dicarbonates preparation

A large combination of different dicarbonates was prepared according 3 different synthesis pathways (Figure 1) to get monomers with different solubilities allowing expecting further modulated leachability. Pathway 1 involved the use of diacyl chlorides, diacides or di-isocyanates to join two glycerol carbonate (GC) moieties (no more described in this paper). The key step of pathways 2 and 3 was the cyclic carbonate groups formation on polyols either obtained by a first condensation of diamines on GC or directly provided by industrial source like the polyglycerol 3 (PG3).

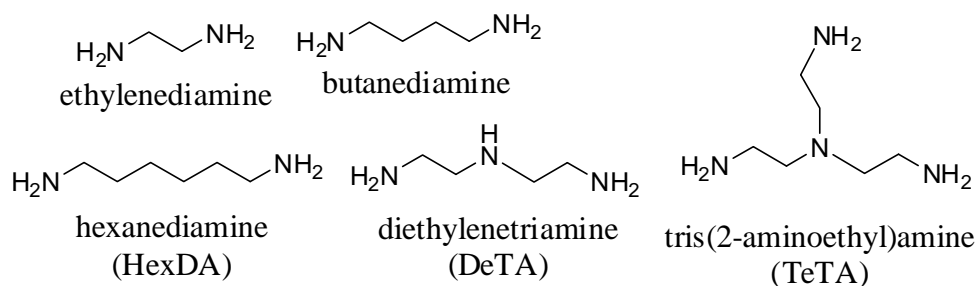
Formation of dicarbonates was studied and checked by FT-IR,  $^1\text{H}$  (Figure 2) and  $^{13}\text{C}$  NMR.

*Figure 2: Effect of the DMC equivalent number on the cyclic carbonate formation on PG3*

The best conditions have been obtained by refluxing in methanol during five hours a catalytic amount of potassium carbonate and three equivalents of DMC. A higher quantity of DMC was not useful because it led to an increased ratio of non cyclic carbonate moiety which was obviously not suitable for the following polymerisation. This ratio between cyclic and not cyclic carbonate groups was also easily monitored by FT-IR experiments since the first showed a vibration band at  $1781\text{ cm}^{-1}$  while the second were detected at  $1750\text{ cm}^{-1}$ .

#### Hydroxypolyurethanes formation

The reaction between dicarbonates and various diamines (Figure 3) have been investigated to find the best and mildest conditions compatible with a polycondensation step performable into the wood shape and taking account as far as possible of a solvent free approach.



*Figure 3: Di- and tri-amines used for polycondensation*

The method conditions development has been carried out with a model monoamine, the n-butylamine, and mainly monitored by FT-IR by giving attention to the cyclic

carbonate carbonyl vibration disappearance and the carbamate carbonyl appearance at  $1704\text{ cm}^{-1}$ .

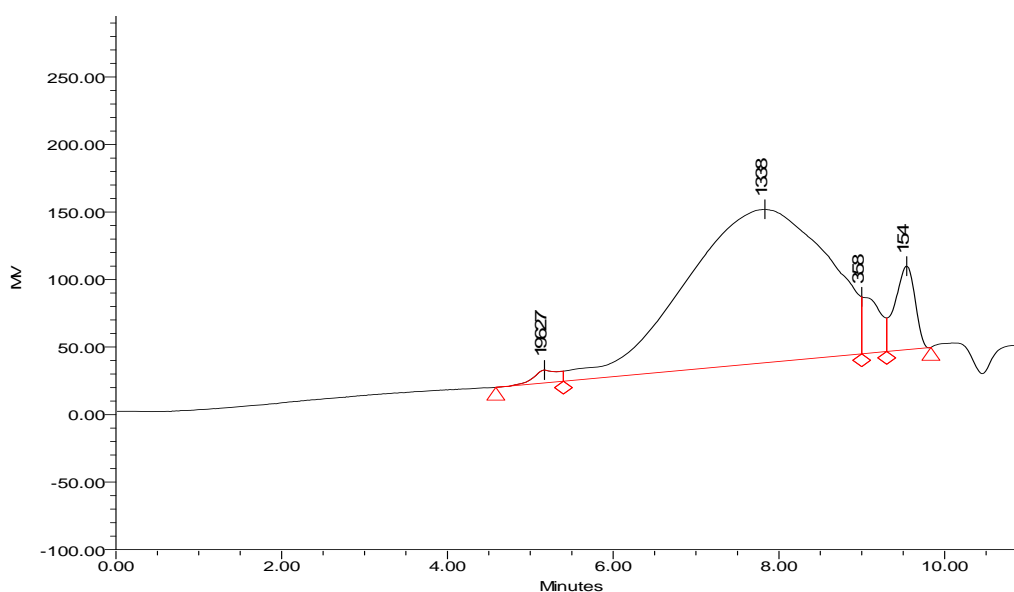
*Table 1. Reaction of polyglycerol carbonate with different amount of n-butylamine*

entry	n-Butylamine (eq) <sup>1</sup>	Weight Gain (%)	Cyclic carbonate (meq/g of CPG3)	$\nu_{\text{C=O}}$ $1781\text{ cm}^{-1}$	$\nu_{\text{C=O}}$ $1704\text{ cm}^{-1}$
a	0.5	12.5	1.7	yes	yes
b	1	21.5	3.0	yes	yes
c	1.25	33.5	4.7	yes	yes
d	1.5	37.5	5.3	no	yes
e	2	43	6.1	no	yes
	4	42.5	6.0	no	yes

<sup>1</sup> calculated on the basis of a dicarbonate of PG3 (DCPG3) with an average molecular weight of 294

Occurring slowly at room temperature, the reaction can be performed in one hour at  $50\text{ }^{\circ}\text{C}$  in methylene chloride or water with slightly less than two equivalents (1.5) of mono amine, meaning that the reaction of amine with cyclic carbonate prevails even in water where hydrolysis of cyclic carbonate may occur. At higher temperature, selectivity of the reaction in water was less important leading to higher amounts of hydrolysis.

These results have been then applied to the di- and triamines to achieve polymerisations. The reaction effectiveness was evaluated by IR, NMR spectroscopy and also size exclusion chromatography (SEC), as illustrated hereafter (Figure 4) with the SEC chromatogram obtained for the reaction product of DCPG3 with one equivalent of diethylenetriamine in water.



*Figure 4: Condensation product of DCPG3 and DeTA (1eq) SEC chromatogram*

### ***Second part: wood treatment***

Beech wood blocks have been treated by a vacuum/pressure process in two steps:

- dicarbonates are impregnated with the appropriated solvent and dried.
- diamines are then impregnated in a convenient solvent, the following drying period at  $50\text{ }^{\circ}\text{C}$  allowing in the same time the polymerisation.

Each step was controlled by FT-IR experiment (Figure 5).

*Figure 5: Typical FT-IR monitoring of the impregnation and drying/polymerization two steps process*

The presence of cyclic carbonate moieties can be attested by the  $1780\text{ cm}^{-1}$  bond indicating the stability of this kind of chemical function during the first drying step. Its transformation during the second drying step into a  $1704\text{ cm}^{-1}$  bond indicates the formation of carbamate groups by reaction with the polyamines.

The polymerisation of the product in wood was quantified by the blocks weight gain (WG) and the dimensional stabilization by the Anti Swelling Efficiency (ASE). Some interesting results are summarised in table 2.

The WG and ASE have been measured before and after a leaching step by boiling water to characterise the treatment resistance to leachability, which is a crucial property for outdoor uses.

The effect as antifungal treatment has also been evaluated by an in vitro 16 weeks exposure of wood blocks to *Poria placenta* colonies on the basis of weight losses (WL) due to fungal decay for both protected and unprotected samples. The results are presented in Table 2 as a ratio between the treated and untreated blocks to homogenise the values obtained with different experiments. Thus, the lowest ratio is obtained for the most efficient protective treatment. In any case, most of the WL absolute values obtained with the treated blocks were below the threshold usually considered as a significant complete protection.

**Table 2: Characterisation of the different pathways of hydroxypolyurethanes formation**

Pathway	Dicarbonate (30% w/w)	Dicarbonate solvent	Amine (30% w/w)	Amine solvent	before leaching		after water leaching		WL Ratio <sup>a</sup>
					WG (%)	ASE (%)	WG (%)	ASE (%)	
1	GC with adipic linker	Acetone	HexDA	CH <sub>2</sub> Cl <sub>2</sub>	31.8	22.3	25.8	18.2	0.175
			DeTA	H <sub>2</sub> O	35.2	30.1	28.7	25.2	0.073
2	GC with HexDA linker	CH <sub>2</sub> Cl <sub>2</sub>	HexDA	CH <sub>2</sub> Cl <sub>2</sub>	21.2	17.5	15.3	12.8	0.248
	GC with DeTA linker	H <sub>2</sub> O	DeTA	H <sub>2</sub> O	29.5	24.3	17.1	16.2	0.203
3	DCPG3	H <sub>2</sub> O	HexDA	CH <sub>2</sub> Cl <sub>2</sub>	39.8	47.2	25.0	33.0	Not done
			DeTA	H <sub>2</sub> O	30.7	62.3	20.0	37.2	0.128
			DeTA+TeTA	H <sub>2</sub> O	38.4	61.3	38.4	55.8	Not done

<sup>a</sup> Ratio between WL after fungal exposure of treated/leached and untreated blocks

For pathways 1 and 3, the measured weight gains after leaching showed good polyurethane retentions into the blocks. In addition, the values were not really different between diamines impregnated in dichloromethane and those used in water which is a very interesting point. The ASE measurements followed the same trend with better results for the way 1 and particularly the way 3, in both cases by using the water soluble diamines. The good values and weak difference between ASE before and after leaching in the case of the mixture DCPG3 with DeTA/TeTA can probably be explained by the reticulation effect of the triethylenetetramine.

The pathway 2 led to worse results, particularly after leaching, and since it was the strategy needing the highest number of preparation steps, it did not appear as a promising pathway.

In most of the cases, the hydroxypolyurethanes were efficient as antifungal treatment by providing a good protecting effect towards the brown rotting *Poria Placenta*. The best results were still obtained with the water soluble polyamines and for the pathways 1 and 3.

## CONCLUSIONS

Utilization of hydroxypolyurethanes gives good preliminary promising results for wood dimensional stabilisation and protection. They can be prepared from existing industrial by-products transformed in one step in reactive monomers, easily impregnable into the wood with aqueous solution among various solvents. The versatility of their synthesis allows the preparation of a wide range of structures with a high modulation of their properties. The polymerisation is carried out by a moderate heating step corresponding to the usual drying step of any wood treatment. The obtained Anti Swelling Effects are interesting and, moreover, the exhibited antifungal capability adds a supplementary advantage to this approach. Further experiments are however necessary to investigate more deeply the potential of such approaches.

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