

*Full Length Research Article***Synthesis and Characterization of Poly(hydroxy)urethane from Polyols for Beech (*Fagus sylvatica*) Wood Impregnation**Vera Junita Sitanggang^{1,*}, Nyoman Jaya Wistara¹, Philippe Gérardin²¹ Department of Forest Products, Faculty of Forestry and Environment, IPB University. Jl. Raya Dramaga, Bogor, 16680, West Java, Indonesia² Laboratory of Research and Wood Material (LERMaB), Faculty of Science and Technology, Université de Lorraine. Inrae, LERMaB, 54000 Nancy, France* Corresponding Author. E-mail address: vera-junita@apps.ipb.ac.id

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ABSTRACT

A non-isocyanate route of polyurethane synthesis based on polyol (xylitol, sorbitol, glycerol, and PG3), alkyl carbonate (DMC and DEC), and diamine (HMDA, EDA, and DETA) was conducted for wood impregnation through in-site polymerization. The structure and mass average molecular weight (M_w) of the polyurethanes were analyzed using FTIR, NMR, and SEC. According to the results, polyurethane synthesis by a two-pot method in water brought cyclic carbonate degradation. The distribution of M_w of the polyurethanes showed that the most satisfying polymer (4380 g/mol) was prepared without solvent. Polyurethanes synthesized in methanol have a higher M_w than that in distilled water. In the same solvent, the use of HMDA resulted in a polymer with higher M_w than that of EDA. One-step wood impregnation in a solvent gave unsatisfactory WPG (12.59–19.71%) and LC (50.36–62.80%). However, one-step impregnation without solvent gave a higher WPG (78.39–87.63%) and a lower LC (19.11–21.25%). It is not feasible to be applied industrially. The two-step impregnation gave WPG (14.89–30.73%) and LC (42.22–56.52%). Wood impregnation using methanol or ethanol as the solvent was more recommended than using an aqueous solution. However, the resistance against leaching needs improvement.

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1. Introduction

Wood is an aesthetic and mostly non-durable material. Endeavors have been done to increase its service life, in which wood preservation with biocide-based chemicals has been the most common (Salminen et al. 2014). However, society's growing concern for environmental quality has encouraged many countries to prohibit using toxic wood preservatives such as CCA. Nontoxic and less leachable or degradable chemicals have been suggested for exterior application (Mubarok et al. 2019; Soulounganga et al. 2004). The finding and application of environmentally benign wood preservatives are becoming paramount.

Both thermal and chemical approaches can improve wood durability. Thermal modification of the internal structure of wood has been proven to improve the dimensional stability and durability of wood, with a diminution of its mechanical properties (Ayrilmis et al. 2011; Hill et al. 2021). The strength loss of wood due to thermal treatment might be brought about by the

degradation of hemicelluloses and modification of lignin structures (Sikora et al. 2022). Chemical treatments brought about comparable effects, except that the mechanical properties of wood could be retained through in-site polymerization (Iaych 2010). In-situ polymerization of wood has also been reported to restrain water penetration, thus preventing wood biodegradation and increasing its dimensional stability (Broda and Hill 2021; Cateto et al. 2008; Gérardin 2016).

Wood consists of cellulose, a linear polymer of many hydroxyl groups capable of forming intra- and inter-molecular hydrogen bonds. Hydrogen bonds relate to bound water responsible for wood shrinking and swelling due to environmental humidity changes (Hill 2006; Sjöstrom 1993). Carbonyl and ethylene are other functional groups capable of forming covalent bonds in wood. Modification of hydroxyl groups has been approached through chemical modification of the cell wall constituent and the formation of a wood-polymer composite (Iaych 2010). This modification has been a prevalent method carried out to increase the properties of wood. A more dimensionally stable wood has resulted from the reaction between hydroxyl groups and various types of isocyanates (Nuryawan and Alamsyah 2018; Rowell 2007).

Wood hygroscopicity is possibly controlled by chemical modification of surface hydroxyl groups and reduced leaching of impregnated chemicals by covalent grafting (reactive impregnation) (Persenaire et al. 2008). In this method, the chemicals used included isocyanates, formaldehyde, alkoxysilanes, and epoxides. These chemicals are also known for their beneficial function against microorganisms without giving up their mechanical properties. Unfortunately, these chemicals also harm the environment (Walsh-Korb 2021).

A wood polymer composite has also been formed through bulk polymerization of the cell wall with an aqueous solution of non-reactive chemicals such as salts, sugars, and glycerol or polyethylene glycol (PEG) (Gérardin 2016; Zhou and Liu 2022). The green chemical pathway of polyurethane synthesis is a promising environmentally friendly process for wood modification (Wołosz et al. 2022). Non-isocyanate route of polyurethane synthesis based on the reactivity of the cyclic carbonate group with amines has been patented by Bernard (2008) and it has been mostly applied to produce polyurethane foams (Heck et al. 2015; Hu et al. 2012; Saldaev et al. 2018; Yang et al. 2021; Zhao et al. 2012). Even though in-site synthesis of poly(hydroxy)urethanes was thought beneficial for cell wall modification, it was realized challenging to gain a high degree of polymerization of polymers through aqueous phase and two-step impregnations of di-carbonate monomers with di- or tri-amines, probably because of the difficulty to control the stoichiometry during impregnation precisely (Brossier et al. 2021; Iaych 2010). The present study was intended to increase the degree of crosslinking in the polyurethane synthesized from xylitol (C5) (Fig. 1) and sorbitol (C6). A more significant number of hydroxyl groups in xylitol and sorbitol was expected to increase the formation of higher crosslinking and branching, thus resulting in a more water-resistant product.

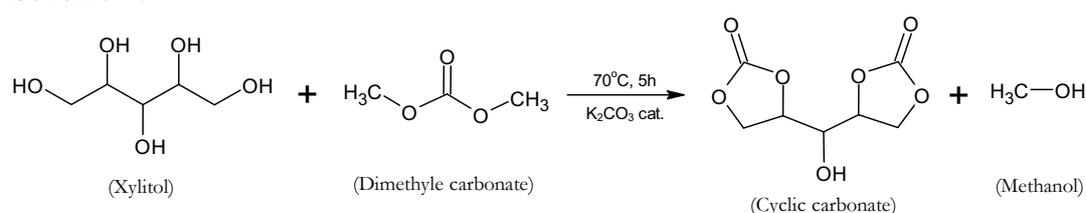
2. Materials and Methods

2.1. Materials and Instruments

The present study emphasized the chemical modification of wood through the in-site formation of polyurethanes based on polyols, alkyl carbonate, and diamine with ethanol, methanol, acetone, and water as the solvents. These solvents are considered environmentally benign chemicals (Brzeska and Piotrowska-Kirschling 2021; Duarte et al. 2014).

The polyols used were glycerol (Carlo Erba Réactifs-SdS France), xylitol (Sigma-Aldrich), sorbitol (Prolabo), and tri-glycerol or polyglycerol-3 (PG3) (Novance-Compiègne, France). Other chemicals used were 1-4 Dioxane (Acros Organics Fisher Scientific France), carbonate compounds (diethyl carbonate (DEC) and dimethyl carbonate (DMC)), amine compounds (diethylene triamine (DETA), hexamethylene diamine (HMDA), and ethylene diamine (EDA)) and K_2CO_3 catalytic (Fluka Sigma Aldrich Chimie SAFC (St. Louis, France)). Preliminary research was carried out on chemical solubility in distilled water, ethanol, methanol, and acetone. The point of the chemical solubility was the minimum ratio of chemical to solvent at complete dissolution.

Scheme 1:



Scheme 2:

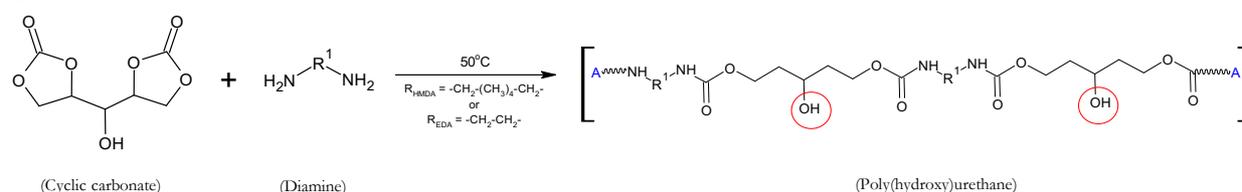


Fig. 1. Synthesis of poly(hydroxy)urethane. Scheme 1: cyclic carbonate formation in the presence of K_2CO_3 catalyst. Scheme 2: polyurethane formation by addition of diamine.

FTIR was used to analyze the functional group on the samples. For the liquid sample, a small amount of the sample was evenly spread to form a thin film between NaCl plates. For a solid sample, approximately 3 mg was mixed with 200 mg of anhydride KBr and thoroughly kneaded in a mortar. The mixture was then placed into a die set and pressed until 700 bar using a pellet press to form a reasonable and compact pellet. This pellet was then scanned using FTIR Spectrometer SPECTRUM 2000 Perkin-Elmer with ATR attachment having spectra range of $4000-400\text{ cm}^{-1}$. The spectrum was read using Spectrum for Windows Version 1.5 ©Perkin-Elmer Ltd 1995.

NMR Spectroscopy was used to examine the molecular structure of the samples. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Bruker AC 200 spectrometer. The sample was first diluted in deuterated chloroform.

Mass average molecular weight (M_w) was determined by Steric Exclusion Chromatography (SEC). The polymer was analyzed by gel permeation chromatography (GPC) after its dissolution in dimethyl formamide (DMF). GPC analysis was performed using a Dionex Ultimate-3000 HPLC system consisting of an autosampler, a detector, and DMF as eluent. The sample was dissolved in DMF ($\approx 20\text{ mg/mL}$), and the solution was filtered through a $0.45\text{ }\mu\text{m}$ filter. The filtered solution ($20\text{ }\mu\text{L}$) was injected into the HPLC system and detected using the refractive index detector. Standard polyethylene glycol (PEG) samples were used to construct a calibration curve. Data were collected and analyzed with Chromeleon software version 6.8 (Dionex Corp., USA). All of these

instrumental measurements were intended to provide information on the quality and structure of the polymer commonly used to analyze polyurethanes.

2.2. Solubility of reagents

It is necessary to test the solubility of each reagent in each solvent because the solvent is the carrier of reagents when impregnated into the wood for the in-site polymerization to occur. The solvent/co-solvent must merely dissolve the reagents without any reaction within them. The reagents tested included the polyols (xylitol, sorbitol, glycerol, and PG3), the alkyl carbonates (DMC and DEC), and the amino compounds (DETA, EDA, and HMDA). The solvents used in this study were distilled water, methanol, ethanol, and acetone. These solvents were chosen based on their relatively low price and low toxicity. Solubility was tested by diluting the reagent in the solvent or co-solvent. The solubility of the reagent was calculated as the ratio of the reagent quantity (A mg) to the amount of solvent needed (B mg) for the complete dilution of the reagent.

2.3. Synthesis of Polyurethane

2.3.1. Two-pot method

The “two pot” method was performed by two successive reactions in a flask equipped with a condenser and a magnetic stirrer. The first reaction was the reaction between polyol and alkyl carbonate. It is known as a trans-carbonatation reaction, which leads to the formation of cyclic carbonate polyol (Bernard 2008). This reaction was performed in an oil bath at 70°C for 5 h in the presence of potassium carbonate (K_2CO_3) as catalyst (0.05 eq.).

The second reaction was the addition of DETA into the system at the end of trans-carbonatation. Theoretically, this reaction occurred at 50°C to form the carbamate (urethane) function (Bernard 2008). Six reactions were performed in different conditions to investigate the feasibility of the synthesis of polyurethane in two pot method. The reactions are listed in **Table 1**.

Table 1. Six different conditions of polyurethane synthesis in two pot method

No.	The reaction I (Trans carbonatation)	Reaction II	Solvent
1	1 eq. of xylitol + 4 eq. of DMC	+ 1 eq. of DETA	Without solvent
2	1 eq. of xylitol + 4 eq. of DMC	+ 2 eq. of DETA	Without solvent
3	1 eq. of sorbitol + 6 eq. of DMC	+ 2 eq. of DETA	Methanol
4	1 eq. of xylitol + 4 eq. of DMC	+ 2 eq. of DETA	Methanol
5	1 eq. of xylitol + 4 eq. of DMC	+ 2 eq. of DETA	Distilled Water
6	1 eq. of xylitol + 4 eq. of DEC	+ 2 eq. of DETA	Distilled Water

2.3.2. One pot method

The “one pot” method was performed by adding 1 eq. of sorbitol, 6 eq. of DMC, and 3 eq. of diamine (i.e., DETA, EDA, and HMDA). The mixture was stirred magnetically in a condenser-equipped flask (under vacuum) or in an opened beaker at 70°C for 5 h with the presence of K_2CO_3 as catalyst (0.05 eq.). The products obtained were then analyzed by FTIR and SEC.

2.4. Wood Impregnation

Wood impregnation was performed on beech (*Fagus sylvatica*) wood. By the previously defined conditions, the impregnation of wood specimens was separated into one-step and two-step

methods. Both of these methods differed in the treated solution. One-step impregnation was performed by simultaneously impregnating a solution containing polyol, alkyl carbonate, and diamine. Seven different conditions of one-step impregnations performed are listed in **Table 2**.

Table 2. Seven different conditions of the one-step impregnation method

No.	Solution	Solvent	Soaking temperature
1	1 eq. of sorbitol + 10 eq. of DMC + 5 eq. of HMDA + catalyst	Water	70°C
2	1 eq. of sorbitol + 10 eq. of DMC + 5 eq. of HMDA + catalyst	Water	20°C
3	1 eq. of sorbitol + 10 eq. of DMC + 5 eq. of HMDA + catalyst	Water	0°C
4	1 eq. of xylitol + 8 eq. of DMC + 4 eq. of HMDA + catalyst	Ethanol	70°C
5	1 eq. of xylitol + 8 eq. of DMC + 4 eq. of HMDA + catalyst	Water	70°C
6	1 eq. of xylitol + 8 eq. of DMC + 4 eq. of HMDA + catalyst	Without Solvent	70°C
7	Patent (Bernard 2008)*	-	-

Notes: *solution was first synthesized using 0,0906 mol of glycerol, 0,182 mol of DMC, 4×10^{-4} mol of phosphazene P1-t-Bu catalyst, and 0,045 mol of HMDA at 100°C under magnetic agitation for one night in a flask equipped with a condenser.

In the case of non-solvent impregnation, all reagents must be pre-polymerized to solubilize them before impregnation. However, when ethanol was the solvent of impregnation, pre-polymerization was held for about 30 min at a temperature of 50°C.

In the two-step method, impregnations were carried out twice with cyclic carbonate of xylitol (prepared by a molar ratio of xylitol/DMC of 1/2) and diamine dissolved in a solvent. In other cases, two-step impregnation was also performed using pure polyol in the first impregnation and alkyl carbonate and diamine in the second impregnation. Four different conditions of two-step impregnations performed are listed in **Table 3**.

Table 3. Five different solutions for the two-step impregnation method

No.	Impregnation I		Impregnation II	
	Reagents	Solvent	Reagents	Solvent
1	Cyclic carbonate of xylitol	Without solvent	HMDA	Distilled water
2	Cyclic carbonate of xylitol	Distilled water	HMDA	Distilled water
3	Cyclic carbonate of xylitol	Ethanol	HMDA	Ethanol
4	Sorbitol	Distilled water	DMC/HMDA(2/1)	Distilled water

Wood impregnation was carried out under the full-cell method. Oven-dried beech (*Fagus sylvatica*) blocks were placed into a beaker in a desiccator, and a vacuum of 0-1 mbar was drawn for about 15 min using a pump. The pressure was then released, allowing the reagent solution to cover and impregnate the wood blocks. After 2 h of soaking (at room temperature or in an oven at 70°C), the blocks were drained and cured at 70°C for 2 days. The weight percentage gain (WPG) was calculated by using the formula:

$$WPG = \frac{m_1 - m_0}{m_0} \times 100\% \quad (1)$$

where m_0 is the oven-dried weight of the untreated wood sample, and m_1 is the oven-dried weight of the impregnated wood sample.

The solutions wasted from impregnation processes were recovered and analyzed by SEC. This waste was equally treated with that of the wood specimens during impregnation, soaking, and

in-site polymerization. The leachability of the chemical was determined according to European Standard NF X41-565 by soaking and shaking the sample in distilled water for three respective durations (1 h, 2 h, and 4 h) by replacing the water in between. The volume of the water used was fivefold the total sample volume. The oven-dried weight of leached wood samples (m_2) was then used to calculate leached chemical (LC) expressed as a percentage of the initial impregnated chemicals calculated by the following formula.

$$LC (\%) = \frac{m_2 - m_1}{m_1 - m_0} \times 100\% \quad (2)$$

3. Results and Discussion

3.1. Results

3.1.1. Solubility of reagents

Xylitol, sorbitol, glycerol, and PG3 were well soluble in distilled water but were not directly in alcohol, except for that xylitol. Xylitol was partly soluble in methanol or ethanol at 50°C. The DMC was well soluble in distilled water at a concentration of about 20% (by weight). DEC required a ternary mixture of water-acetone-methanol (2:1:1 by volume) to be soluble to a concentration of 37.5% (by weight). The DETA, HMDA, and EDA were highly soluble in all solvents. Even HMDA, which is solid at room temperature and has characteristics associated with its hydrophobic carbon chain of 6 atoms, could be solubilized in water, ethanol, and acetone. It can be explained by the effect of the NH_2 function, which gives a hydrophilic character (Duchanois 2011). Distilled water can substantially dissolve the mixtures of all the reagents with a concentration of about 20% (by weight). In the case of using the DMC, it was possible to break the emulsion formed (by the excess of DMC) by adding a small amount of methanol or ethanol to obtain a single-phase solution.

3.1.2. Synthesis of polyurethane

3.1.2.1. Two-pot method without solvent

In a non-solvent two-pot reaction, initially, xylitol was insoluble in DMC. At the end of this reaction, the one-phase liquid obtained was then analyzed by FTIR. The spectrogram of the FTIR is shown in **Fig. 2**. The important functional group characteristic in **Fig. 2** was the existence of cyclic carbonate with a vibration band of 1778 cm^{-1} . The band of 3003 cm^{-1} belonged to $-\text{OH}$, while the band of 2853 cm^{-1} was to $-\text{CH}$.

The addition of DETA in two different amounts (i.e., 1 eq. and 2 eq.) resulted in products with their FTIR spectra shown in **Fig. 3**. Both spectra show a band at about 1704 cm^{-1} as a characteristic of the $\text{C}=\text{O}$ bond and a band at 3340 cm^{-1} as a characteristic of $-\text{NH}$ bond. These confirm the formation of a carbamate (urethane) function. Vibration bands visible at 1750 cm^{-1} and 1790 cm^{-1} in the spectrum with 1 eq. of DETA indicate the presence of an excess of the DMC and the cyclic carbonate of xylitol, respectively. On the other hand, in the spectrums with 2 eq. of DETA, the characteristics of DMC or carbonate of xylitol were absent and only indicated the presence of urethane function. At this polymerization reaction's end, the product was completely liquid with no solid residue. This result leads to the possibility of a non-solvent polyurethane (carbamate) synthesis.

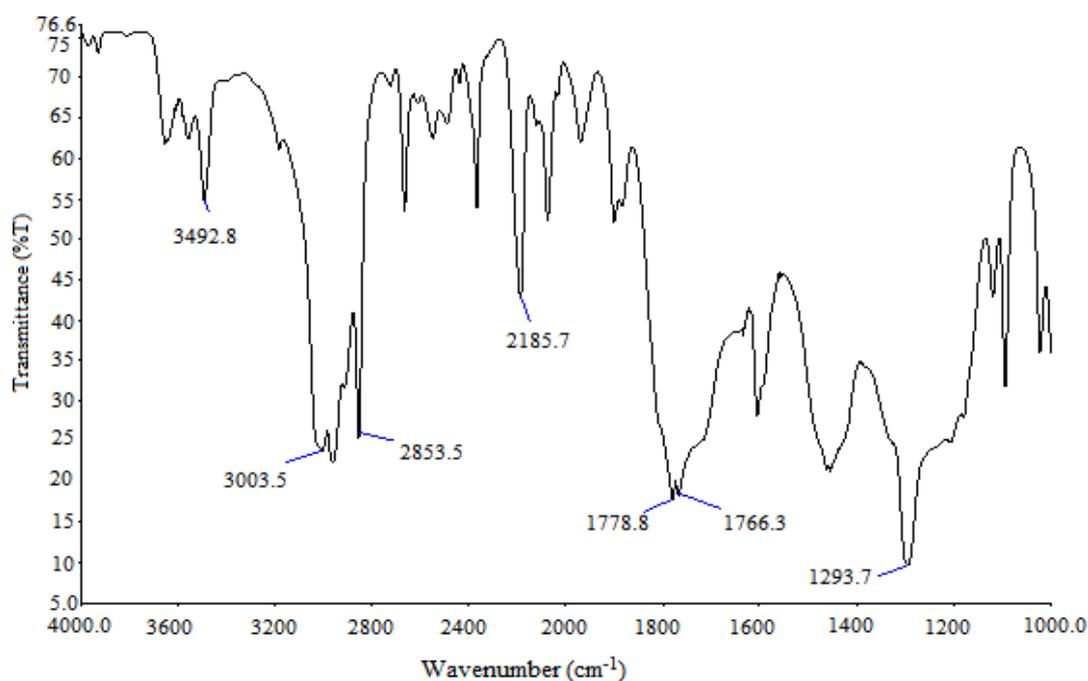


Fig. 2. FTIR spectrum of the reaction products between xylitol and dimethyl carbonate (DMC).

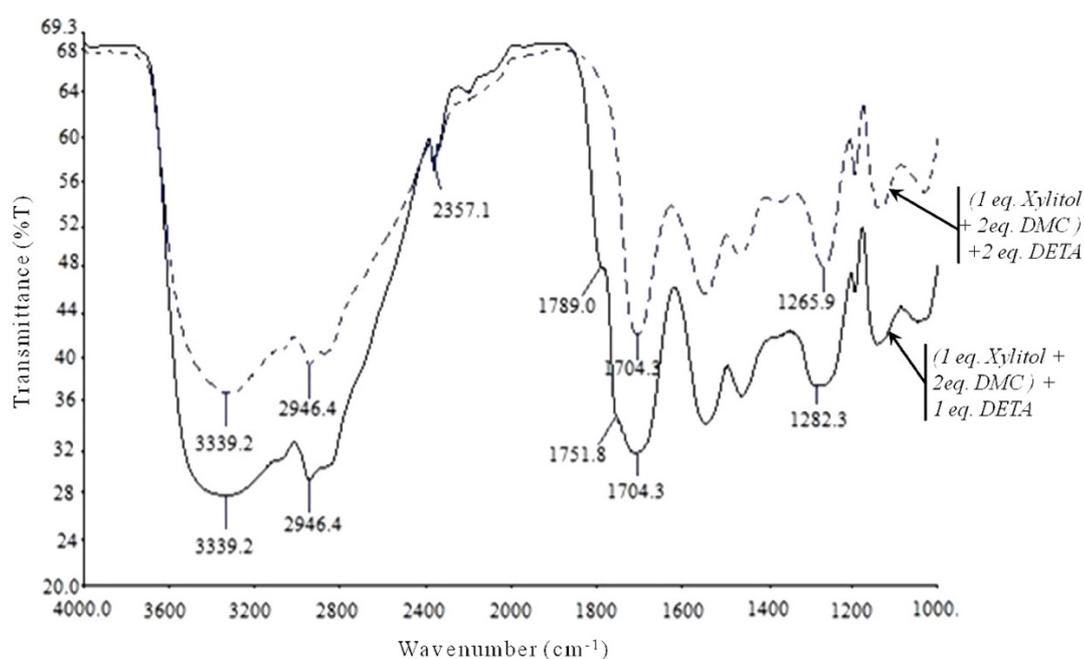


Fig. 3. FTIR spectra of the reaction products from an equivalent of xylitol, two equivalents of DMC, and 1 and 2 equivalents of DETA.

3.1.2.2. Two-pot method in distilled water and alcohol

The spectra shown in **Fig. 4** indicate the FTIR spectrogram of two pot reactions in distilled water and methanol. It shows that the elongation band of the cyclic carbonate at 1780-1790 cm^{-1} was absent from the FTIR spectra of trans-carbonation products when the reaction was carried out in the water. Instead, the presence of a vibration band at 2116 cm^{-1} indicates the possibility of degradation of cyclic carbonate during this reaction. On both spectra, the band at 3300 cm^{-1} corresponds to the elongation of the $-\text{OH}$ bond; it may be of polyol or the alcohol (methanol). And the band at 1640 cm^{-1} is the harmonic of it. Harmonic vibration is a combination of a molecule's

fundamental vibration, which is affected by the complexity of the overlapping/multiple of the frequency absorbed (Li et al. 2020; Pineda-Herrera 2006). The weak band at 2940 cm^{-1} corresponds to the elongation vibration of the $-\text{CH}$ bond.

After adding the DETA to these reactions, no carbamate function was found in the reactions in water. This result confirmed the degradation of cyclic carbonate in the aqueous medium. Nevertheless, a carbamate functional group at 1700 cm^{-1} appeared in methanol during the reaction (Fig. 5). The FTIR spectra of the cyclic carbonate formation using DEC and DMC (Fig. 4) show similar characteristics. However, the use of DMC was more straightforward than that of DEC since the latter required a solvent mixture of water, acetone, and methanol to dissolve. The FTIR spectrum of reaction with xylitol as polyol also resulted in a relatively similar structure product to sorbitol as a polyol in the same condition (Fig. 4 and Fig. 5).

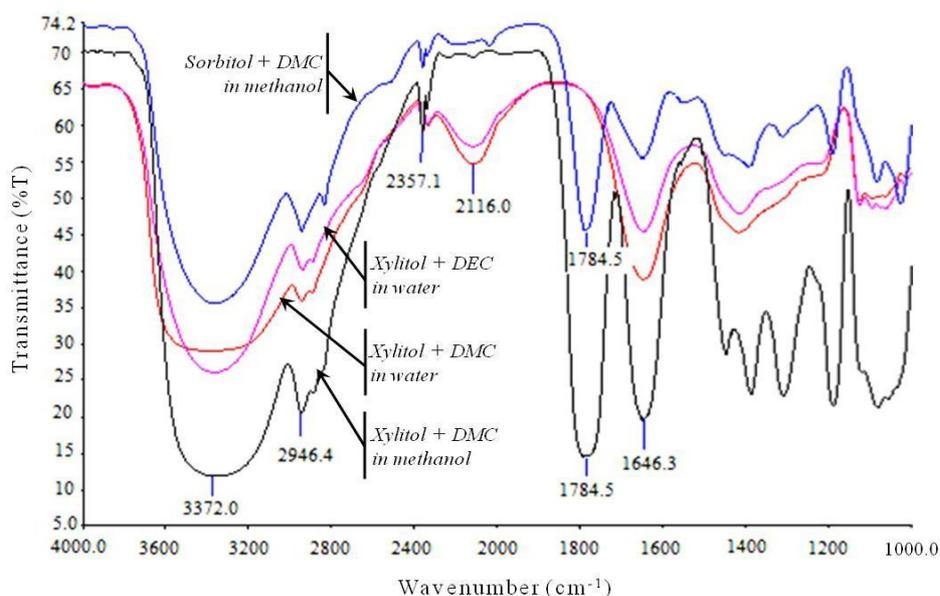


Fig. 4. The FTIR spectra of the cyclic carbonate of xylitol and sorbitol prepared in distilled water and methanol.

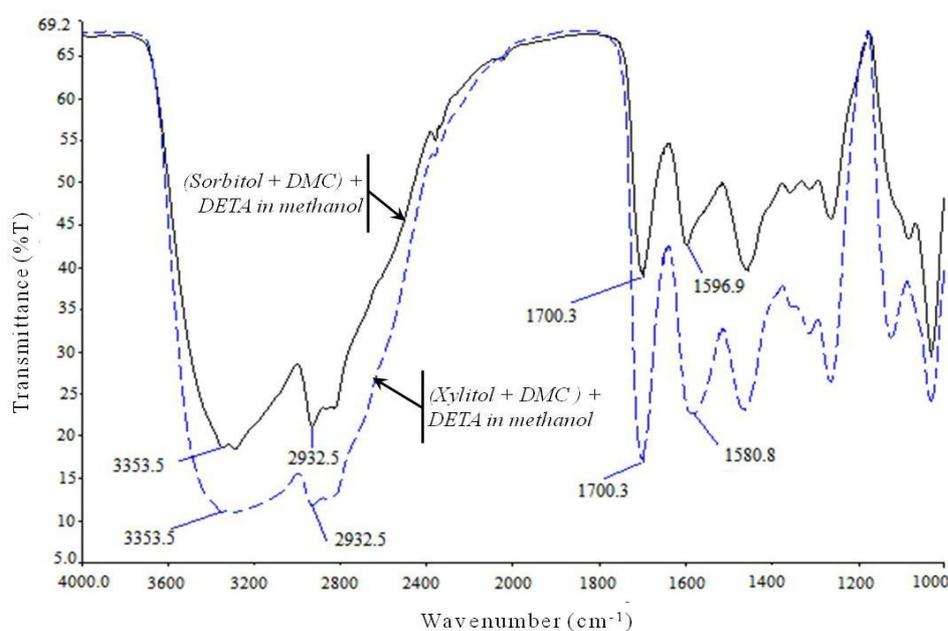


Fig. 5. FTIR spectra of the polyurethane found from reactions of xylitol and sorbitol prepared in methanol.

3.1.2.3. One-pot method

One pot reaction of polyurethane formation using different diamines gave FTIR spectra, as shown in **Fig. 6**. The vibration at 1700 cm^{-1} and 1540 cm^{-1} correspond to the presence of carbamate function. This band is visible in all reactions performed.

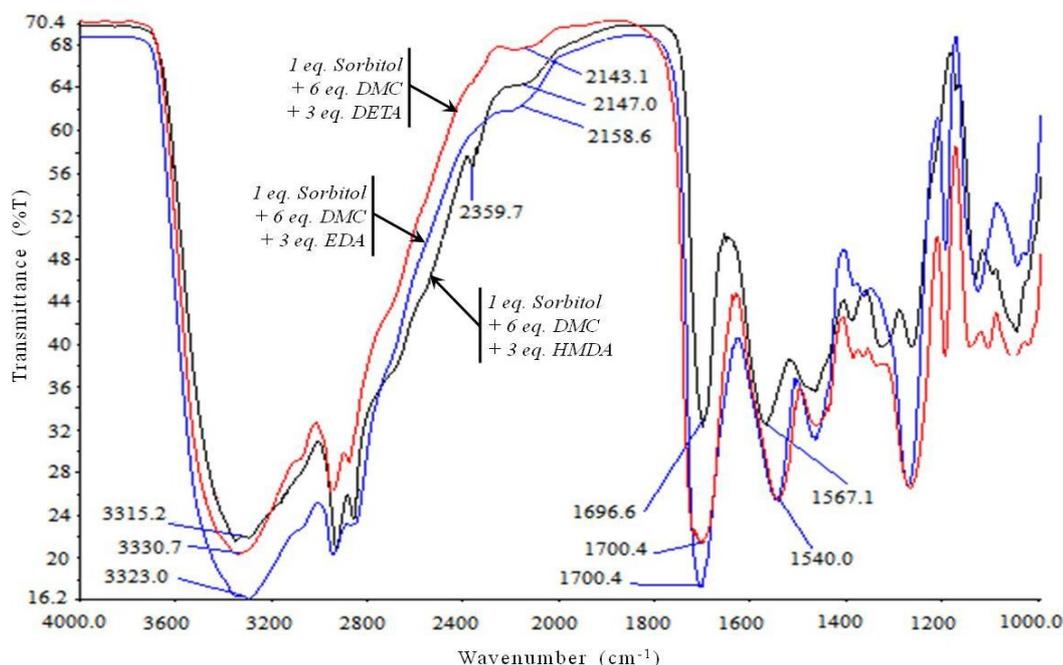


Fig. 6. FTIR spectra of one pot reactions performed using different diamines. The visual appearance of polymers varies considerably by the diamine used.

The use of HMDA resulted in a solid product that was less water-soluble compared to that resulted from the use of EDA and DETA. Therefore, HMDA was used for further polyurethane synthesis. The best ratio of DMC/HMDA for each polyol according to the physical appearance of the polymer produced is listed in **Table 4**. These ratios are then used to prepare the solution for wood impregnation.

Table 4. The best ratio of DMC/HMDA for each polyol

Polyol (one equivalent)	Number of equivalents	
	DMC	HMDA
Sorbitol	10	5
Xylitol	8	4
PG3	6	3

3.1.3. Average molecular mass distribution

The distribution of the mass average molecular weight (M_w) of the resulting polyurethanes was determined by steric exclusion chromatography (SEC), and the results are listed in **Table 5**. The most satisfying polymers with M_w of 4380 g/mol were prepared without solvent. Reaction in water-produced polymers with M_w less than 750 g/mol. **Table 5** indicates that polyurethane synthesis in methanol was better than that in water. In the same solvent, the use of HMDA resulted in a polymer with a higher molecular weight than that of EDA.

3.1.4. Wood impregnation

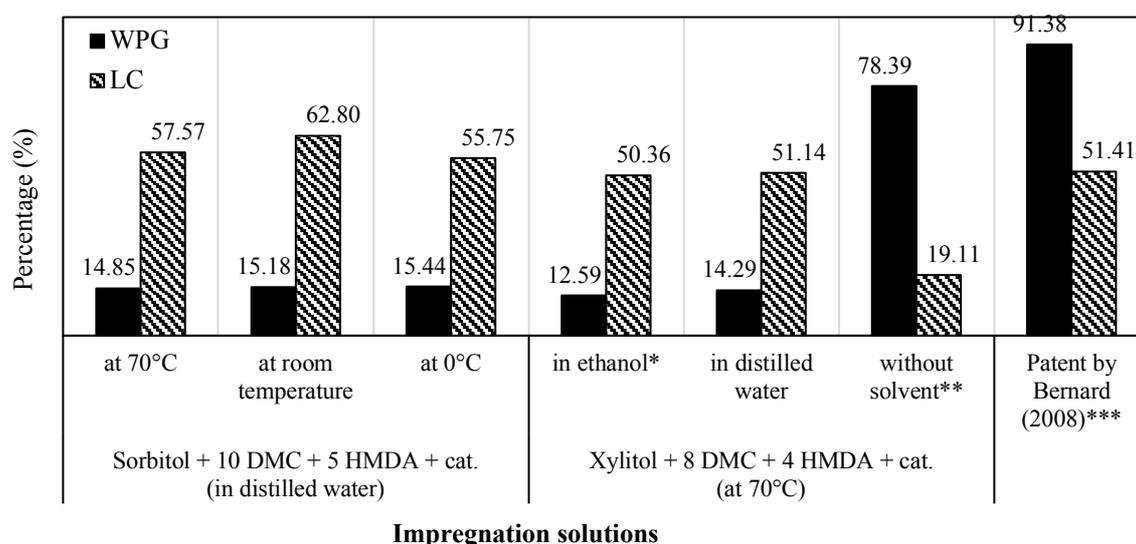
3.1.4.1. One step impregnation

An impregnation using sorbitol, DMC, and HMDA in water under room temperature was carried out and gave WPG of about 15.18%. The LC obtained under these conditions was 62.80 % (Fig. 7), possibly due to the low degree of polymerization (M_w of the solution was 118 g/mol). At the end of this impregnation, a white solid substance was formed. The chemical structure and stoichiometry of this substance were then identified by FTIR spectroscopy, SEC, and NMR. The FTIR spectrum is shown in Fig. 8. The SEC analysis indicated that the substance's average molar mass (M_w) was 283 g/mol. This substance's ^1H - and ^{13}C -NMR spectra are shown in Fig. 9 and Fig.10.

Table 5. Molecular weight (M_w) of polyurethanes determined by SEC

Condition					M_w (g/mol)	Degree of Polymerization
Polyol (1 eq.)	Eq. of carbonate	Diamine	Solvent	Method		
PG3	6 DMC	3 HMDA	Distilled water	one pot	651	1.06
Sorbitol	10 DMC	5 HMDA	Distilled water	one pot	748	1.02
Xylitol	8 DMC	4 EDA	Distilled water	one pot	603	1.01
Xylitol	8 DMC	4 EDA	Methanol	one pot	1923	1.05
Xylitol	8 DMC	4 HMDA	Methanol	one pot	3404	1.19
Xylitol	8 DMC	EDA/HMDA	Distilled Water/ Methanol	one pot	674	1.01
Xylitol	4 DMC	2 HMDA	Without solvent	one pot	4380	1.28
Xylitol	8 DMC	4 HMDA	Ethanol	two pot	2344	1.05
Patent (Bernard 2008)*					1408	1.01

Notes: *solution was first synthesized using 0,0906 mol of glycerol, 0,182 mol of DMC, 4×10^{-4} mol of phosphazene P1-t-Bu catalyst, and 0,045 mol of HMDA at 100°C under magnetic agitation for one night in a flask equipped with a condenser.



Notes :

* prepolymerization for about 30 min at 50°C

** prepolymerization for about 1 h at 70°C

*** solution was synthesized first by using 0,0906 mol of glycerol, 0,182 mol of DMC, 4×10^{-4} mol of phosphazene P1-t-Bu catalyst, and 0,045 mol of HMDA at 100°C under magnetic agitation for one night in a flask equipped with a condenser

Fig. 7. Weight percent gain (WPG), percentage of leached chemicals (LC) of the polymer obtained from impregnation in a one-step method.

The presence of carbamate functions is indicated by the bands of 1700 and 1540 cm^{-1} in **Fig. 8**. The $^1\text{H-NMR}$ spectrum confirmed a well-defined structure, corresponding to a dimethyl-1,6-hexanedylbis carbamate or named di-urethane, formed by the secondary reaction between DMC and HMDA (**Fig. 9**). The peak at 3.787 ppm corresponds to two methyl groups ($-\text{CH}_3$) of DMC. The peaks at 2.68 ppm, 1.49 ppm, and 1.36 ppm were assigned to the molecule's three types of methylene groups (Advanced Industrial Science and Technology (AIST) n.d.). The $^{13}\text{C-NMR}$ spectrum of the substance confirmed the structure of diurethane as assumed by $^1\text{H-NMR}$ (**Fig. 10**).

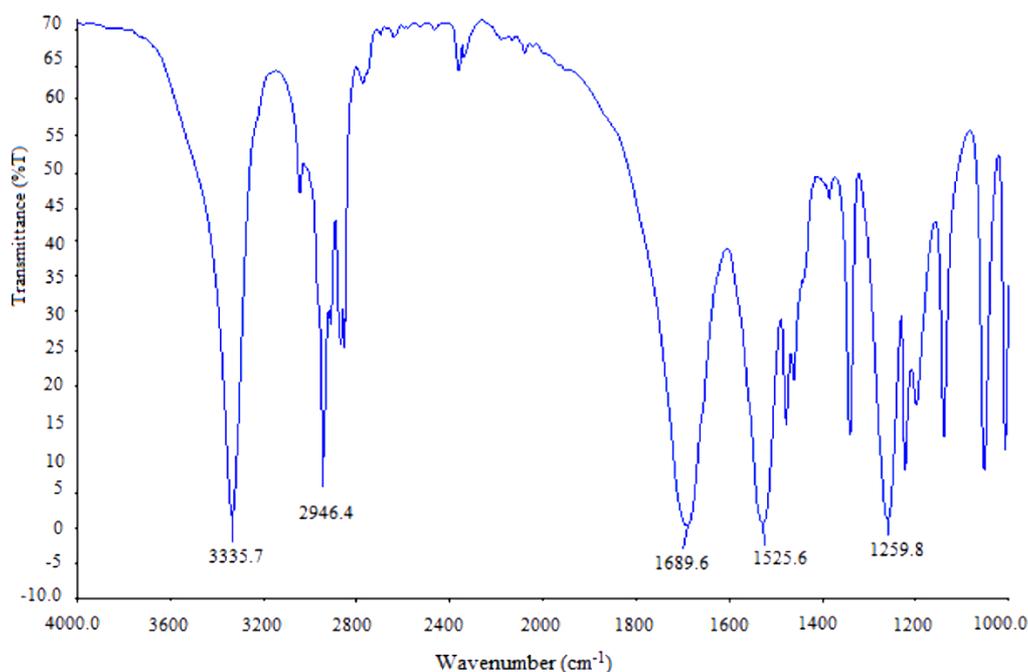


Fig. 8. FTIR spectrum of the diurethane produced by the reaction between DMC and HMDA.

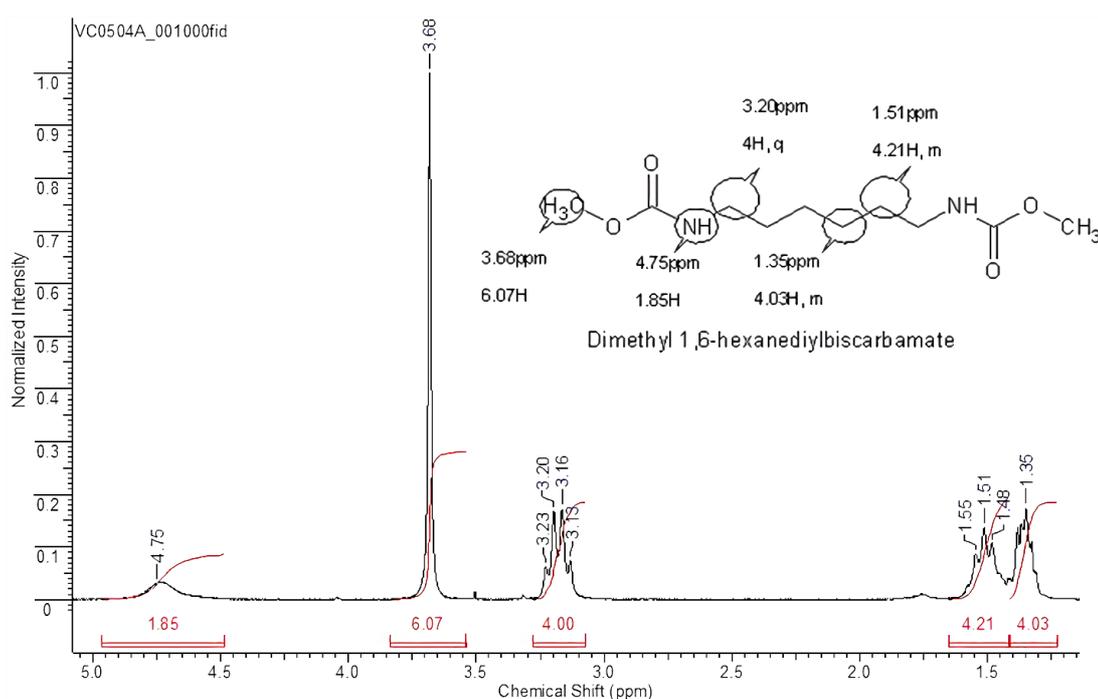


Fig. 9. The $^1\text{H-NMR}$ spectrum of the diurethane produced by the reaction between DMC and HMDA.

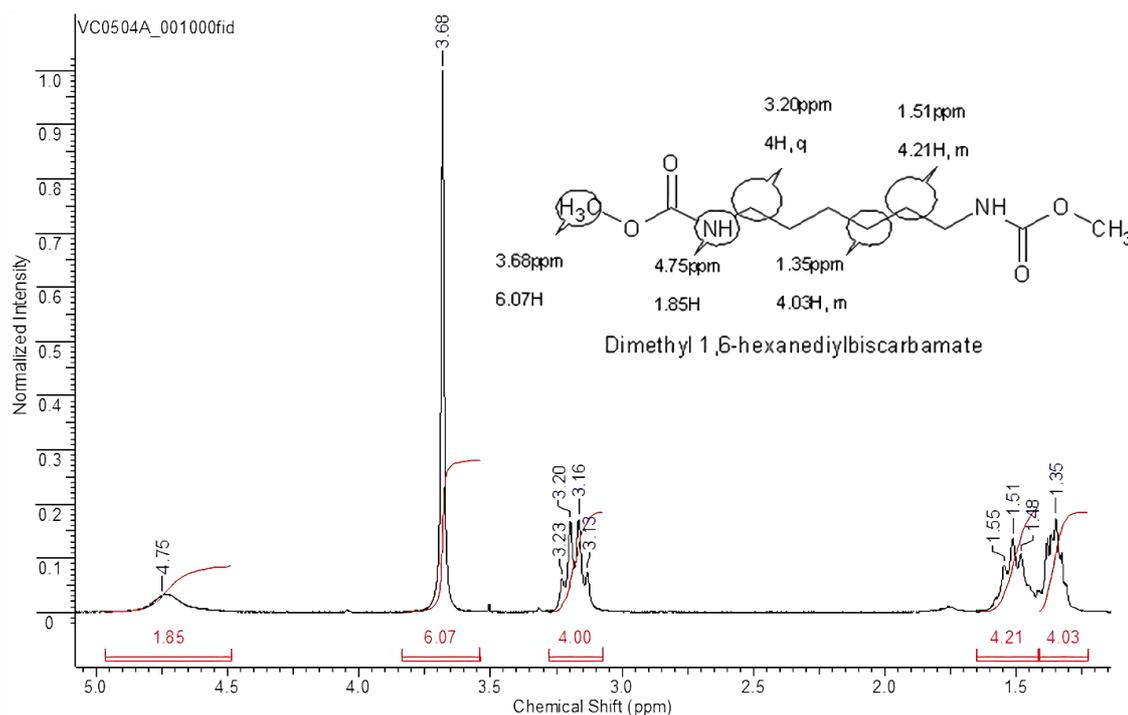


Fig. 10. The ^{13}C -NMR spectrum of the diurethane produced by the reaction between DMC and HMDA.

The secondary reaction between DMC and HMDA in the aqueous solvent was undesirable since the DMC was expected to react initially with polyol before reacting with HMDA. In addition, with an average molar mass of 283 g/mol, the diurethane hindered the penetration of the reagents into the wood. Unfortunately, the secondary reaction between DMC and HMDA could not be avoided by changing the solvent or placing the reaction under acidic or basic conditions.

To avoid the secondary reaction of diurethane formation, several impregnations were performed at different soaking temperatures of 0°C and 70°C. These impregnations gave WPGs 15.18% and 15.44%, respectively, and LCs above 55%. The poor result was confirmed by the low degree of polyurethane polymerization synthesized in water, as shown in **Table 5**. These confirmed the occurrence of diurethane-producing secondary reactions between DMC and HMDA. It also indicated that diurethane with low molecular weight was formed preferentially during the reaction in an aqueous medium rather than in an alcoholic medium.

Non-solvent, in water and ethanol, impregnation of xylitol, DMC, and HMDA was performed. Non-solvent impregnation increased WPG by up to 78.39%, and only 19.11% were degraded after leaching. However, the resulting WPGs and LCs from the impregnation of reagents in water and ethanol were unsatisfactory. As a comparison, a non-solvent impregnation (100% concentration) was also performed based on the patented finding of [Bernard \(2008\)](#), which resulted in a WPG of 91.38%. The resulting LC of 51.41% was even less encouraging. These results are currently unexplainable from the perspective of the water solubility of poly(hydroxy)urethane.

3.1.4.2. Two-step impregnation

Several two-step impregnations were performed, and the resulting data of their WPGs and LCs are shown in **Fig. 11**. The first two-step impregnation was carried out by the cyclic carbonate

of xylitol impregnation (with no solvent) and subsequently followed by the impregnation of diamine in water. The WPG₁ (6.82 %) was found to quadruplicate WPG₂ (23.91 %) in two-step impregnation with the absence of solvent (**Fig. 11**). The impregnated cyclic carbonate of the first step left inadequate space for the retention of the second step HMDA impregnation. Due to the water-soluble nature of cyclic carbonate and HMDA, its impregnation tended to increase leaching.

The two-step impregnation in water and ethanol resulted in a total weight gain of 28.92% and 23.27%, respectively, and the LCs of 43.08 % and 42.22 %, respectively. It is a noteworthy finding because the one-step impregnation in water resulted in a lower WPG (approximately 15%) and LC of about 55% (**Table 5**). Separated transcarbonatation reaction (cyclic carbonate synthesis) and diamine addition possibly prevented the formation of diurethane through a secondary reaction.

Separated impregnations of sorbitol and DMC/HMDA gave a low WPG of 14.89 %. This poor result has been previously explained in one-step impregnation with the same reagents. However, the LCs of the two-step impregnation with sorbitol and DMC/HMDA were lower (54.42 %) than that of the one-step impregnation (62.80 %), as shown in **Fig. 7**.

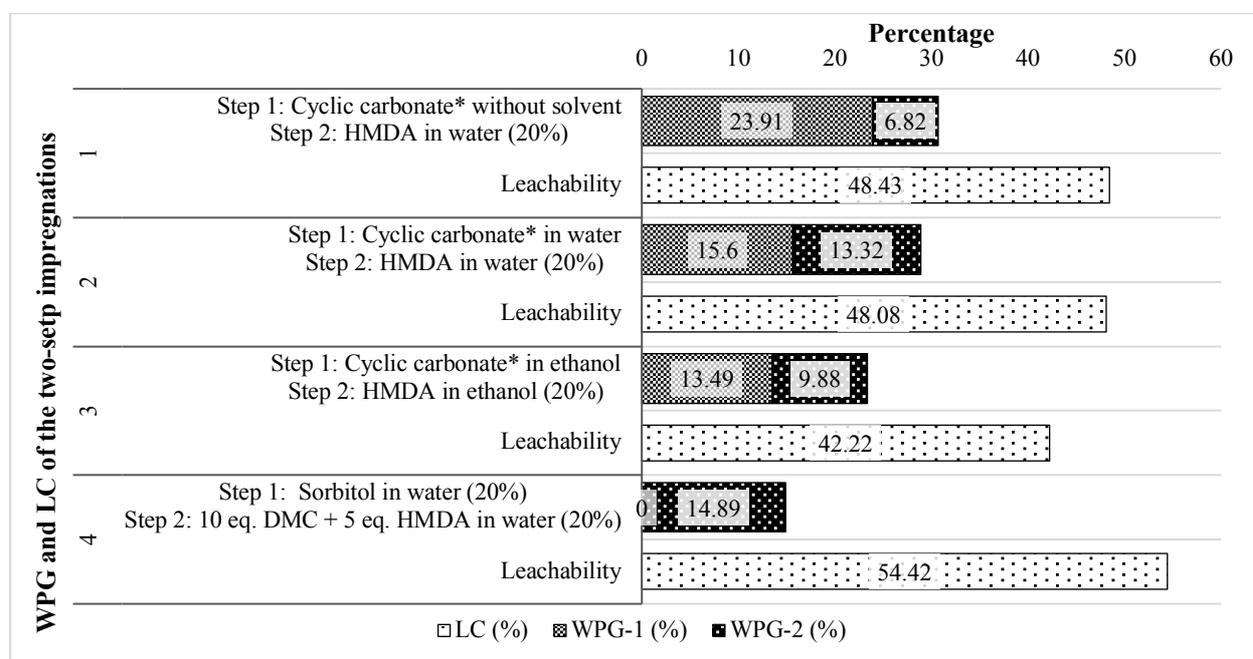


Fig. 11. Weight Percent Gain (WPG) and percentage of leached chemicals (LC) of the two-step impregnation.

3.2. Discussion

3.2.1. Synthesis of polyurethane

The cyclic carbonate formation of xylitol in distilled water faced inconvenience, i.e., degradation of the cyclic carbonate. The temperature difference gave no significant result. It is, therefore, necessary to carry out the synthesis of polyurethane in a non-aqueous solvent. This solvent can prevent the degradation of cyclic carbonate and dissolve the reagents to control the stoichiometry of the reagents and avoid the formation of small oligomers (Iaych 2010). Alcohols are the best candidate to meet these conditions. Duchanois (2011) reported that cyclic carbonate is more reactive with primary amines in water. Therefore, polyurethane synthesis was considered in

a single step (one-pot method) by adding all of the reagents (polyol, alkyl carbonate, diamine, and catalyst) simultaneously.

As resulted in **Fig. 6**, the less-soluble characteristic of the product from the use of HMDA was thought to be due to the HMDA hydrophobic character (Duchanois 2011). This result was why the HMDA was chosen for the subsequent works in a non-isocyanate synthesis of polyurethanes.

To simulate the one-pot method concerning the impregnation, some reactions were performed using a simple open beaker to allow the evaporation of methanol formed during the reaction at 70°C and event produce the desired polymer directly. This method allows polymer formation from the first hour of the reaction. However, the resulting polymer was still soluble in water and thus failed to produce a less leachable polymer that could be applied in wood. The evaporation of DMC during the reaction might indicate its poor solubility. The DMC has a boiling point close to the water (90°C); its slow evaporation during the reaction may change the stoichiometry of the reaction and reduce the degree of polymerization.

3.2.2. Average mass distribution

Diamine structure was reported to influence the molecular weight of the polymer, in which the higher the molecular weight of diamine, the higher the molecular weight of the resulting polymer (Froidevaux et al. 2016). The use of HMDA was then more recommended in comparison with the EDA.

The polyurethane derived from the reaction without solvent gave a high molecular weight polymer of 4380 g/mol. The synthesis of polyurethane using the one-pot method has been recommended by the patent of Bernard (2008). Unfortunately, impregnating wood without solvent is not applicable industrially (Cornille et al. 2017). It is also challenging to maintain the stoichiometry of the reaction during impregnation and in-site polymerization (Duchanois 2011; Rudin and Choi 2013). The synthesis of polyurethane through a one-pot method using xylitol, DMC, and HMDA in methanol produced polymer with M_w of 3404 g/mol. The synthesis of polyurethane with the same reagents in ethanol through the two-pot method gave a lower M_w of 2344 g/mol (**Table 5**). However, the same reagents processed without solvent showed a higher molar mass of 4380g/mol. Polymers with higher molar mass indicated higher mechanical properties, thus (Wolosz et al. 2022).

Related to the length of the polyols, polyurethane synthesized by using sorbitol, DMC, and HMDA in distilled water resulted in a higher M_w (748 g/mol) than by using xylitol, DMC, and EDA in the same solvent (603 g/mol). The previous research investigated that removing the shorter polyols produced a polymer with a higher molar mass (Iuliano et al. 2020). The addition of the longer-chain diols to the poly(hydroxy)urethane synthesis could produce a higher degree of polymerization of polymer (Ionescu 2016; Maisonneuve et al. 2015). However, Wolosz et al. (2022) stated that the molar ratio of the reagents has no bearing on the molar mass of a polymer.

A polymer derived from a reaction recommended by the patent of Bernard (2008) gave low molecular weight polymers, despite the presence of urethanes, cyclic carbonate, and hydroxy-urethanes. It is confirmed by the product obtained from a reaction with cyclic carbonate of xylitol and HMDA using phosphazene P1-t-Bu as a catalyst. The product obtained has a molecular weight of 1408 g/mol. Indeed, the synthesis of polyurethane in the two-pot method reduces the degree of

polymerization (DP) and leads to larger leaching or smaller oligomers (**Table 5** and **Fig. 11**) ([Duchanois 2011](#)).

3.2.3. Wood impregnation

Fig. 7 and **Fig. 11** show that the highest WPGs and lowest LCs belonged to the impregnation without solvent (with a concentration of 100%). [Duchanois \(2011\)](#) explained that the polymer synthesized without solvent is more linear than the polymer synthesized in a solvent. A linear polymer is more resistant to leaching than a branched polymer ([Patachia and Croitoru 2016](#)).

Fig. 7 also shows poor results from the one-step impregnations using water as a solvent. The low WPGs (about 15%) and the high LCs (above 55%) represent an unacceptable result for industrial application. This poor result may be caused by the secondary reaction's inevitable formation of diurethane, even with changing the temperature. The only interaction between the diurethane and wood is Van der Waals bonds, made by NH (carbamate) functions. The diurethane was, therefore, easily removed by water during leaching ([Duchanois 2011](#)). The poor result was confirmed by the low degree of polyurethane polymerization formed, as shown in **Table 5**.

4. Conclusions

Synthesis of polyurethane using no solvent gives a polymer with a high degree of polymerization. Since it is not practically applicable in charge with wood impregnation, the impregnation using methanol or ethanol as the solvent is more recommended by comparing the impregnation with an aqueous solution. However, the impregnation results by polymers obtained from an alcoholic solution face a problem when used outdoors due to their leachability. Synthesis of polyurethane in an aqueous medium allows degradation of cyclic carbonate and thus reduces the urethane function produced. However, synthesis in an alcoholic medium gives larger polyurethane. Because of these results, testing these polymers against termites and fungi on wood specimens treated and leached is crucial. These results allow us to validate these results and whether to continue the research towards a potential application of wood chemical modification. In the context of developing a green method for wood modification, the results obtained in this work are very encouraging for future industrial use. Despite the unsatisfying results of impregnation, this synthesis can find its place at the industrial level, in the order of an environmentally friendly method, entering a general context of sustainable development and low toxicity to humans.

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