SYNTHESIS OF POLY(HYDROXY)URETHANE FROM POLYOL AND LIQUEFIED SPRUCE BARK FOR WOOD IMPREGNATION

VERA JUNITA BR SITANGGANG

POST GRADUATE SCHOOL
BOGOR AGRICULTURAL UNIVERSITY
BOGOR
2013
Hak Cipta Dilindungi Undang-Undang

1. Dilarang mengutip sebagian atau seluruh karya tulis ini tanpa mencantumkan dan menyebutkan sumber:
   a. Pengutipan hanya untuk kepentingan pendidikan, penelitian, penulisan karya ilmiah, penyusunan laporan, penulisan kritik atau tinjauan suatu masalah.
   b. Pengutipan tidak merugikan kepentingan yang wajar IPB.
2. Dilarang mengumumkan dan memperbanyak sebagian atau seluruh karya tulis ini dalam bentuk apapun tanpa izin IPB.
THESIS STATEMENT AND SOURCES OF INFORMATION

I hereby declare that the thesis with the title SYNTHESIS OF POLY(HYDROXY)URETHANE FROM POLYOL AND LIQUEFIED SPRUCE BARK FOR WOOD IMPREGNATION is my own work with direction and guidance of the supervising committee and has not been submitted in any form in any university or other institution, unless the relevant agencies (Bogor Agricultural University (IPB) and University of Lorraine (France)). Sources of information derived from the published or unpublished works, are listed in the references summarized at the end of the thesis.

Bogor, July 23rd, 2013

Vera Junita br Sitanggang
NIM E251100061
SUMMARY

SITANGGANG VERA JUNITA. Synthesis of Poly(Hydroxy)Urethane from Polyol and Liquefied Spruce Bark for Wood Impregnation. Supervised by NYOMAN J. WISTARA (Bogor Agricultural University – Indonesia) and PHILIPPE GÉRARDIN (University of Lorraine – France).

The finding and application of environmentally benign wood preservatives is becoming paramount. Nontoxic and less leachable or degradable chemical have been suggested for exterior application. Polyurethanes synthesized through a green chemical pathway is very promising environmentally friendly wood modification processes. In this study, non-isocyanate route of polyurethane synthesis based on polyol (i.e. xylitol, sorbitol, liquefied spruced bark, glycerol and PG3), alkyl carbonate (i.e. DMC and DEC) and diamine (i.e. HMDA, EDA and DETA) was realized for wood impregnation through in-site polymerization. The structure and mass average molecular weight ($M_w$) of polyurethanes synthesized and impregnated were then analyzed by using FTIR, NMR and SEC.

According to the results, synthesis of polyurethane by two pot method in water brought to cyclic carbonate degradation. The using of DEC in transcarbonatation reaction in two pot method gave similar characters of FTIR spectrum to the use of DMC, however the used of DMC was simpler than that of DEC. The synthesis of polyurethane by one pot method using different diamines confirmed the presences of carbamate function as analyzed by FTIR. However, the visual appearance of polymers produced showed that the use of HMDA as diamine resulted a solid product that was less water-soluble compared to that resulted from the used of EDA and DETA.

The distribution of mass average molecular weight ($M_w$) of polyurethanes synthesized determined by SEC showed that the most satisfying polymer with $M_w$ of 4380 g/mol was prepared without solvent. The reaction in water produced polymers with low $M_w$ (less than 750 g/mol). Polyurethanes synthesized in methanol has higher $M_w$ than that in water. In the same solvent, the use of HMDA resulted in a polymer with higher $M_w$ than that of using EDA.

Wood impregnations using one step method using solvent gave unsatisfactory WPG (about 12.59 – 19.71 %) and LC (about 50.36 – 62.80 %). One step impregnation without solvent gave higher WPG (about 78.39 – 87.63 %) and lower LC (19.11 – 21.25 %). However, wood impregnation without solvent is not feasible to be applied industrially. In other hands, five conditions of two step impregnations performed gave WPG of about 14.89 – 30.73 % and LC of about 42.22 – 56.52 %. In the case of two step impregnations without solvent, the first impregnation left inadequate space for the retention of the second step. It corresponds rather to leaching. Moreover, wood impregnation in two step faced a constrain of reaction stoichiometry. Since it is not applicable in charge with wood impregnation using methanol or ethanol as the solvent is more recommended by comparing with impregnation with an aqueous solution. However, it needs improvement on its resistance against leaching when used outdoor.

Keywords: polyurethane, polyol, alkyl carbonate, diamine, liquefied bark, wood impregnation
RINGKASAN

SITANGGANG VERA JUNITA. Sintesis Poly(hidroksi)uretan dari Polyol dan Kulit Spruce Terliquifikasi untuk Bahan Impregnasi Kayu. Dibimbing oleh I NYOMAN J. WISTARA (Institut Pertanian Bogor, Indonesia) dan PHILIPPE GÉRARDIN (University of Lorraine, France).

Berdasarkan banyak penelitian mengenai pengawetan kayu belakangan ini, bahan kimia tidak beracun dan tidak mudah tercuci atau terdegradasi banyak direkomendasikan untuk aplikasi eksterior. Sintesis polyuretan menggunakan bahan kimia ramah lingkungan sangat menjanjikan untuk dikembangkan dalam bidang modifikasi kayu. Pada penelitian ini, dilakukan sintesis polyuretan tanpa isocyanate, yaitu menggunakan polyol (xylitol, sorbitol, produk liquefaksi kulit kayu, gliserol dan PG3), karbonat alkil (DMC dan DEC), dan diamin (HMDA, EDA dan DETA) untuk polimerisasi in-situ kayu melalui impregnasi. Struktur kimia dan berat molekul massa rata-rata ($M_w$) dari poly uretan yang disintesis kemudian dianalisis menggunakan FTIR, NMR dan SEC.

Berdasarkan data yang diperoleh, diketahui bahwa penggunaan air sebagai pelarut berakibat pada degradasi karbonat siklik pada sintesis polyuretan dengan metode two pot. Dibanding dengan DEC, penggunaan DMC lebih direkomendasikan karena tidak membutuhkan kombinasi pelarut untuk reaksi dan kedua memberikan karakteristik spektrum FTIR hampir sama. Sintesis polyurethan dengan metode one pot menggunakan diamin yang berbeda menunjukkan adanya fungsi karbamat saat dianalisis menggunakan FTIR. Namun demikian, pada pelarut yang sama, penggunaan HMDA sebagai diamin menghasilkan $M_w$ polimer lebih besar.

Distribusi $M_w$ polyuretan yang diperoleh menunjukkan bahwa $M_w$ polimer terbesar, sebesar 4380 g/mol, dihasilkan dengan sintesis tanpa pelarut. Sintesis dalam media air menghasilkan polimer yang memiliki $M_w$ rendah (kurang dari 750 g/mol). Polyuretan yang disintesis dalam metanol memiliki $M_w$ lebih besar dibandingkan yang dihasilkan dengan menggunakan air sebagai pelarut.

Impregnasi kayu dengan metode one step memberikan nilai WPG rendah (sekitar 12,59 – 19,71%) dan LC tinggi (sekitar 50,36 – 62,80%). Impregnasi one step tanpa pelarut memberikan WPG lebih tinggi (sekitar 78,39 – 87,63) dan LC lebih rendah (19,11 – 21,25%). Namun, impregnasi kayu tanpa menggunakan pelarut tidak efisien untuk diterapkan dalam skala industri. Di sisi lain, impregnasi two step memberikan nilai WPG lebih tinggi (sekitar 14,89 – 30,73%) dan LC sekitar 42,22 – 56,52%. Pada impregnasi two step, impregnasi pertama menghabiskan reaksi yang dalam pada impregnasi kedua dan berakibat juga pada tinggi LC. Impregnasi kayu dengan metode two step juga sulit untuk dianalisis stoikiometri. Dengan demikian, impregnasi one step menghasilkan pelarut methanol atau etanol lebih direkomendasikan jika dibandingkan dengan impregnasi menggunakan pelarut air. Namun demikian, dibutuhkan penelitian lebih lanjut untuk meningkatkan ketahanannya terhadap pencucian air (leaching) untuk dapat direkomendasikan untuk aplikasi di luar ruangan.

Kata kunci : polyuretan, polyol, karbonate alkil, diamin, liquefaksi kulit kayu, impregnasi
SYNTHESIS OF POLY(HYDROXY)URETHANE FROM POLYOL AND LIQUEFIED SPRUCE BARK FOR WOOD IMPREGNATION

VERA JUNITA BR SITANGGANG

Thesis
as a prerequisite to obtain
Master of Science degree in
Forest Products Technology Program

POST GRADUATE SCHOOL
BOGOR AGRICULTURAL UNIVERSITY
BOGOR
2013
Penguji Luar Komisi: Prof. Dr. Ir. H. Dodi Nandika, MS
Thesis title: Synthesis of Poly(Hydroxy)Urethane from Polyol and Liquefied Spruce Bark for Wood Impregnation

Name: Vera Junita br Sitanggang
NIM: E251100061

Approved,
Supervising Commission

p.p. Dr. Philippe Gérardin

I Nyoman J. Wistara, Ph.D.
19631231 198903 1 027

Prof. Dr. Wayan Darmawan, M.Sc.
19960212 199103 1 002

Endorsed by,
Head of Study Program of Forest Products Technology

Prof. Dr. Ir. Wayan Darmawan, M.Sc.
19960212 199103 1 002

Dean of Post Graduate School

Prof. Dr. H. Dahirul Syah, MSc Agr.
19650814 199002 1 001

Date of Exam: 26 Juli 2013
Date of Graduation: 22 Aug 2013
Thesis title: Synthesis of Poly(Hydroxy)Urethane from Polyol and Liquefied Spruce Bark for Wood Impregnation

Name: Vera Junita br Sitanggang

NIM: E251100061

Approved,

Supervising Commission

p.p. Dr. Philippe Gérardin

I Nyoman J. Wistara, Ph.D.
19631231 198903 1 027

Prof. Dr. Wayan Darmawan, M.Sc.
19960212 199103 1 002

Endorsed by,

Head of Study Program of Forest Products Technology

Dean of Post Graduate School

Prof. Dr. Ir. Wayan Darmawan, M.Sc.
19960212 199103 1 002

Prof. Dr. Ir. Dahrul Syah, MSc.Agr.
19650814 199002 1 001

Date of Exam: Date of Graduation:
Bogor Agricultural University

Hak cipta milik IPB ( Institut Pertanian Bogor)
FOREWORD

Praise and thankfulness I pray to Jesus for His interfering in completing this paper. The topic chosen in this study which was conducted in January to May 2012 is synthesis of green wood preservative, with title Synthesis of Poly(Hydroxy)Urethane from Polyol and Liquefied Spruce Bark for Wood Impregnation.

I would like to express my deep gratitude to Dr. Phillipe Gérardin and Dr. Stéphane Dumarçay (University of Lorraine), and I Nyoman Wistara, Ph.D (Bogor Agricultural University), for guiding me during this research in theory and practice. Also Dr. Xavier Duret who had guided me at the beginning of this research in ENSTIB, Epinal, France. And my partner, Christopher Garry, I thank for the patience, compactness and helps throughout the research, especially for motivation and jokes to make this research more interesting. I would also thank to Dr. Bintang Simangunsong for all support and advices during this thesis working.

I also thank the technical team with all the staffs in Laboratory of Studies and Researches on Wood Materials (LERMaB), Faculty of Science and Technology, University of Lorraine, France.

I thank my friends from “Un Chant Nouveau” church and R’Espèrence association, who accepted me into their family and encouraged, supported and motivated me throughout my study in Nancy, France.

I also thank all my friends trainees; Novitri Hastuti, Solafa Salman, Joël Hamada, Debbia Derridj, Shafiaa Meheeni, Julien Faux, Jinbo Hu who has created many great memories during working in LERMaB.

A special thank I offer to all my friends from Post Graduate School of IPB, all the classmates; Irsan Alipraja, Rentry Augusty Nurbaity, Sonia Somadona, Meylida Nurrachmania, Yusup Amin, Kurnia Prasetyo, Renny Purnawati, Novitri Hastuti, Muthmainah Rusly, and Adrin Lobang. I thank for all the support and great friendship during our study, for all sharing willingness to hear and understand each other.

And last, I offer a thankful heart for my fiance, Tumpal Trimatua Pangaribuan who has a humble heart to love, to pray, to support and to live a life with me. My family; mom, dad, bro Robert, bro Sandy, bro Roy, to whom I proud of, I thank for all support, pray, love and motivation during whole time of thesis working. All my best friends from The Breakers and The Breakers Junior, I thank for the motivation and pray to finish my master study well.

Hopefully, this paper useful.

Bogor, July 23rd, 2013

Vera Junita br Sitanggang
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vi</td>
</tr>
<tr>
<td>ABBREVIATIONS</td>
<td>vi</td>
</tr>
<tr>
<td>1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2 METHODOLOGY</td>
<td>2</td>
</tr>
<tr>
<td>Materials and Instruments</td>
<td>3</td>
</tr>
<tr>
<td>Bark Liquefaction</td>
<td>3</td>
</tr>
<tr>
<td>Solubility of Reagents</td>
<td>4</td>
</tr>
<tr>
<td>Synthesis of Polyurethane</td>
<td>4</td>
</tr>
<tr>
<td>Wood Impregnation</td>
<td>5</td>
</tr>
<tr>
<td>Chemical Leachibility</td>
<td>7</td>
</tr>
<tr>
<td>3 RESULTS</td>
<td>7</td>
</tr>
<tr>
<td>Liquefaction of Spruce Bark</td>
<td>7</td>
</tr>
<tr>
<td>Solubility of Reagents</td>
<td>7</td>
</tr>
<tr>
<td>Synthesis of Polyurethane</td>
<td>8</td>
</tr>
<tr>
<td>Average Molecular Mass Distribution</td>
<td>12</td>
</tr>
<tr>
<td>Wood Impregnation</td>
<td>12</td>
</tr>
<tr>
<td>4 DISCUSSION</td>
<td>19</td>
</tr>
<tr>
<td>Liquefied Spruce Bark</td>
<td>19</td>
</tr>
<tr>
<td>Synthesis of Polyurethane</td>
<td>19</td>
</tr>
<tr>
<td>Average Mass Distribution</td>
<td>20</td>
</tr>
<tr>
<td>Wood Impregnation</td>
<td>21</td>
</tr>
<tr>
<td>5 CONCLUSION</td>
<td>21</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>22</td>
</tr>
<tr>
<td>AUTHOR BIOGRAPHY</td>
<td>24</td>
</tr>
</tbody>
</table>
LIST OF TABLES

1. Six different conditions of two pot method 5
2. Ten different conditions of one-step impregnations 5
3. Five different conditions of two-step impregnations 6
4. Liquefaction yield of spruce bark 7
5. Best ratio of DMC / HMDA for each polyol 11
6. Molecular weight ($M_w$) of polyurethanes determined by SEC analysis 12

LIST OF FIGURES

1. Synthesis of poly(hydroxy)urethane: Cyclic carbonate formation in the presence of $K_2CO_3$ catalyst (Scheme 1). Polyurethane formation by addition of diamine (Scheme 2). 2
2. FTIR spectrum of the reaction products between xylitol and DMC 8
3. FTIR spectra of the reaction products from an equivalent of xylitol, 2 equivalents of DMC and 1 and 2 equivalents of DETA 9
4. The FTIR spectra of the cyclic carbonate of xylitol and sorbitol prepared in water and methanol. 10
5. The FTIR spectra of the polyurethane found from reactions of xylitol and sorbitol prepared in methanol. 10
6. FTIR spectra of one pot reactions performed by using different diamines 11
7. Weight percent gain (WPG), percentage of leached chemicals (LC), and the molecular weight ($M_w$) of the polymer obtained from impregnation in one-step method. 13
8. FTIR spectrum of the diurethane produced by the reaction between DMC and HMDA 14
9. $^1$H-NMR spectrum of the diurethane produced by the reaction between DMC and HMDA 15
10. $^{13}$C-NMR spectrum of the diurethane produced by the reaction between DMC and HMDA 16
11. Weight Percent Gain (WPG) and percentage of leached chemicals (LC) of the two-step impregnations 18

ABBREVIATIONS

DEC : dietyl carbonate
DETA : diethylene triamine
DMC : dimethyl carbonate
EDA : ethylene diamine
eq : number of molar equivalent
FTIR: Fourier Transform Infrared
HMDA: hexamethylene diamine
K$_2$CO$_3$: potassium carbonate
KBr: potassium bromide
LB: Liquefied spruce bark
LC: percentage of leached chemicals (in wood) (%)
LERMaB: Laboratory of Studies and Researches on Wood Materials
M$_w$: Weight average molecular weight (g/mol)
NMR: Nuclear Magnetic Resonance
PD: polydispersity (ratio $M_w$ to $M_n$)
PG3: tri-glycerol or polyglycerol-3
SEC: Steric Exclusion Chromatography
WPG: Weight Percent Gain (%)
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. However, the increasing concern of society on environmental quality has encouraged many countries to prohibit the use of toxic wood preservative such as CCA. Nontoxic and less leachable or degradable chemical have been suggested for exterior application (Soulounganga et al. 2004). The finding and application of environmentally benign wood preservatives is becoming paramount.

Wood durability can be improved by both thermal and chemical approaches. Thermal modification of the internal structure of wood has been proven to improve the dimensional stability and durability of wood, nevertheless with diminution of its mechanical properties (Ayrilmis et al. 2011). Strength loss of wood due to thermal treatment might be brought about by the degradation of hemicelluloses and modification of lignin structures (Brosse et al. 2010). Chemical treatments brought about comparable effect, except that the mechanical properties of wood could be retained through in-site polymerization (Iaych 2010). In-site polymerization of wood has also been reported restraining water penetration, thus prevented wood biodegradation and increased its dimensional stability (Soulounganga et al. 2004; Cateto et al. 2008; Persenaire et al. 2004).

Wood consists of cellulose, a linear polymer that consists of many hydroxyl groups capable of forming intra- and inter-molecular hydrogen bonds. Hydrogen bonds relate to bound water that is responsible to wood shrinking and swelling due to the change of environmental humidity (Sjöstrom 1993; Hill 2006). Carbonyl and ethylene are other types of functional group capable of forming covalent bonds present in wood. Modification of hydroxyl groups has been approached through chemical modification of the cell wall constituent and the formation of wood-polymer composite (Iaych 2010). This modification has been a very common method carried out to increase the properties of wood. A more dimensionally stable wood has been resulted from reaction between hydroxyl groups and various types of isocyanates (Cateto et al. 2008).

Persenaire et al. (2004) controlled wood hygroscopicity by chemical modification of surface hydroxyl groups and reduced leaching of impregnated chemicals by covalent grafting (reactive impregnation). Chemicals used in the first method included anhydrides, isocyanates, formaldehydes, alkoxysilanes, and epoxides. Meanwhile, the later method was used to protect wood against microorganisms without giving up its mechanical properties. The formation of wood polymer composite has been done also through bulk polymerization of cell wall with aqueous solution of non-reactive chemicals such as salts, sugars and glycerol or polyethylene glycol (PEG) (Cateto et al. 2008). Green chemical pathway of polyurethanes synthesis is very promising environmentally friendly processes applicable for wood modification. Non isocyanate route of polyurethane synthesis based on the reactivity of cyclic carbonate group with amines has been patented by Bernard (2008) and it has been mostly applied to produce polyurethane foams (Zhang et al. 2007; Hu et al. 2011). Even though in-site synthesis of poly(hydroxy)urethanes was thought beneficial for cell wall
modification, it was realized difficult to gain high DP of polymers through aqueous phase and two-step impregnations of dicarbonates monomers with di- or tri-amines, probably because of the difficulty to precisely control the stoichiometry during impregnation (Iaych 2010). The present study was intended to increase the degree of crosslinking in the polyurethane synthesized from xylitol (C5) (Figure 1) and sorbitol (C6). Greater number of hydroxyl groups in xylitol and sorbitol was expected to increase the formation of higher crosslinking and branching, thus resulted in a more water-resistant products.

\[ \text{Xylitol} + \text{DMC} \xrightarrow{70^\circ C, 5h} \text{Cyclic carbonate} + \text{Methanol} \]

Figure 1. Synthesis of poly(hydroxy)urethane. Cyclic carbonate formation in the presence of \( \text{K}_2\text{CO}_3 \) catalyst (Scheme 1). Polyurethane formation by addition of diamine (Scheme 2).

In the present works, polyurethane was also synthesized by substituting polyols with liquefied bark. Bark is an inexpensive and abundant renewable natural source with interesting chemical components. It is specific tissues protecting the tree against external aggressions such as biological attacks caused by fungi and insects, and also against the physical and chemical degradation from loading activities, sun, temperature and humidity (Duret et al. 2009). The structure and composition of bark are different to those of wood. It contains less polysaccharides, but higher in extractives and lignin. Bark is a valuable source of energy in industry and raw material for liquefaction products applicable for wood quality improvement. Dominated by extractives, lignin, polyphenols, polysaccharides, and tannins, bark is rich in hydroxyl groups of aromatic units and polysaccharides potentially form a urethane function (Zhao et al. 2012). In this study, bark of Spuce (\( \text{Picea abies} \)) was chosen as the raw material of liquefaction.

2 METHODOLOGY

The present studies were emphasized on the chemical modification of wood through in-site formation of polyurethanes based on polyols, alkyl carbonate and diamine with ethanol, acetone and water as the solvents. These solvents are considered as environmentally benign chemicals.
Materials and Instruments

The polyols used were glycerol (Carlo Erba Réactifs-SdS France), xylitol (Sigma-Aldrich), sorbitol (Prolabo), PG3 (Novance-Compiègne, France) and liquefied Spruce (*Picea abies*) bark (donated by École Nationale Supérieure des Technologies et Industries du Bois – ENSTIB, France). Other chemicals used were 1-4 Dioxane (Acros Organics Fisher Scientific France), carbonate compounds (DEC and DMC), amine compounds (DETA, HMDA and EDA) and K₂CO₃ catalytic (Fluka Sigma Aldrich Chimie SAFC (St. Louis, France)). Preliminary research on chemicals solubility in distilled water, ethanol, methanol, and acetone was carried out. The point of chemical solubility is the minimum ratio chemical to solvent at complete dissolution.

FTIR was used to analyze the functional group of the samples. For liquid sample, small amount of sample was evenly spread to form a thin film between NaCl plates. For solid sample, approximately 3 mg of sample was mixed with 200 mg of anhydride KBr and thoroughly kneaded in a mortar. This pellet was then scanned by using FTIR Spectrometer SPECTRUM 200 Perkin-Elmer with ATR attachment having spectra range of 4000-400 cm⁻¹. The spectrum was read by using Spectrum for Windows Version 1.5 ©Perkin-Elmer Ltd 1995.

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

Mass average molecular weight (Mₐ) was determined by Spheric Exclusion Chromatography (SEC). The polymer was analyzed by gel permeation chromatography (GPC) after its dissolution in DMF. GPC analysis was performed using a Dionex Ultimate-3000 HPLC system consisting of an autosampler, a detector and using dimethyl formamide (DMF) as eluent. The sample was dissolved in DMF (≈ 20 mg/mL), and the solution was filtered through a 0.45 μm filter. The filtered solution (20 μL) was then injected into the HPLC system and was 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.

Bark Liquefaction

Oven dried spruce (*Picea abies*) bark with particle size of 0.4-0.5 mm was liquefied with glycerol as the solvent, and held in a three-neck round-bottom flask equipped with mechanical stirrer and thermometer. The weight ratio of bark powder to the glycerol (solid to liquid ratio – S/L ratio) were 1 : 4 and 1 : 7, and 3% sulfuric acid (based on the glycerol weight) was used as catalyst. The reaction was carried out at 180°C in an oil bath for 120 minutes. The bark content of liquefaction was either 10 grams or 50 grams.
After the predetermined reaction time, the reaction was stopped by cooling the flask in an ice bath to an internal temperature of 60°C. The viscous product was then diluted with dioxane/water (80/20) co-solvent before filtering. Filtration was carried out with a dry filter paper in a vacuumed suction Buchner funnel. The residue was heated at 103°C to oven dry and it was weighed upon drying. The filtrate was evaporated at 80°C to remove dioxane and water. The resulting viscous filtrate is the product of liquefaction. The liquefaction yield was calculated by the following formula:

\[ R_l \% = 100 - \frac{m_2}{m_1} \times 100 \]

Where \( R_l \) is the yield of liquefaction (%); \( m_1 \) is the mass of bark particle (g); and \( m_2 \) is the mass of solid residu (g).

**Solubility of Reagents**

It is necessary to test the solubility of each reagent in each solvent, due to the solvent is the carrier of reagents when impregnated into the wood for the in situ 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. The choice of these solvents was based on their relative low price and low toxicity.

Test of solubility was carried out by diluting the reagent in the solvent or co-solvent. The solubility of the reagent was simply calculated as the ratio of the reagent quantity (A mg) to the quantity of solvent needed (B mg) for complete dilution of the reagent.

**Synthesis of Polyurethane**

**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 transcarbonatation reaction, which leads to the formation of cyclic carbonate polyol (Bernard 2008). This reaction performed in an oil bath at 70°C for 5 hours in the presence of potassium carbonate (\( \text{K}_2\text{CO}_3 \)) as catalyst (0.05 eq.).

The second reaction was the addition of DETA into the system at the end of transcarbonatation. Theoretically, this reaction occurred at temperature of 50°C to form the carbamate (urethane) function (Bernard 2008).

In order to investigate the feasibility of synthesis of polyurethane in two pot method, six reactions were performed in different conditions. The reactions were listed in Table 1.
Table 1. Six different conditions of two pot method

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction I (Transcarbonation)</th>
<th>Reaction II</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1 eq. of xylitol + 4 eq. of DMC</td>
<td>+ 1 eq. of DETA</td>
<td>Without solvent</td>
</tr>
<tr>
<td>2.</td>
<td>1 eq. of xylitol + 4 eq. of DMC</td>
<td>+ 2 eq. of DETA</td>
<td>Without solvent</td>
</tr>
<tr>
<td>3.</td>
<td>1 eq. of sorbitol + 6 eq. of DMC</td>
<td>+ 2 eq. of DETA</td>
<td>Methanol</td>
</tr>
<tr>
<td>4.</td>
<td>1 eq. of xylitol + 4 eq. of DMC</td>
<td>+ 2 eq. of DETA</td>
<td>Methanol</td>
</tr>
<tr>
<td>5.</td>
<td>1 eq. of xylitol + 4 eq. of DMC</td>
<td>+ 2 eq. of DETA</td>
<td>Water</td>
</tr>
<tr>
<td>6.</td>
<td>1 eq. of xylitol + 4 eq. of DEC</td>
<td>+ 2 eq. of DETA</td>
<td>Water</td>
</tr>
</tbody>
</table>

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) simultaneously. The mixture was stirred magnetically in a condenser equipped flask (under vacuum) or an opened-beaker at 70°C for 5 hours with the presence of K₂CO₃ as catalyst (0.05 eq.). The products obtained were then analysed by FTIR and SEC.

Wood Impregnation

In accordance to the previously defined conditions, the impregnation of wood specimens was separated into one-step and two-step method. Both of these methods were differed by the treated solution. One-step impregnation was performed by simultaneously impregnating solution containing polyol, alkyl carbonate and diamine. Ten different conditions of one-step impregnations performed were listed in Table 2.

Table 2. Ten different conditions of one-step impregnations

<table>
<thead>
<tr>
<th>No.</th>
<th>Solution</th>
<th>Solvent</th>
<th>Soaking temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1 eq. of sorbitol + 10 eq. of DMC + 5 eq. of HMDA + catalyst</td>
<td>Water</td>
<td>70</td>
</tr>
<tr>
<td>2.</td>
<td>1 eq. of sorbitol + 10 eq. of DMC + 5 eq. of HMDA + catalyst</td>
<td>Water</td>
<td>20</td>
</tr>
<tr>
<td>3.</td>
<td>1 eq. of sorbitol + 10 eq. of DMC + 5 eq. of HMDA + catalyst</td>
<td>Water</td>
<td>0</td>
</tr>
<tr>
<td>4.</td>
<td>1 eq. of xylitol + 8 eq. of DMC + 4 eq. of HMDA + catalyst</td>
<td>Ethanol</td>
<td>70</td>
</tr>
<tr>
<td>5.</td>
<td>1 eq. of xylitol + 8 eq. of DMC + 4 eq. of HMDA + catalyst</td>
<td>Water</td>
<td>70</td>
</tr>
<tr>
<td>6.</td>
<td>1 eq. of xylitol + 8 eq. of DMC + 4 eq. of HMDA + catalyst</td>
<td>Without Solvent</td>
<td>70</td>
</tr>
<tr>
<td>7.</td>
<td>1 eq. of LB + 6 eq. of DMC + 3 eq. of HMDA + catalyst</td>
<td>Without Solvent</td>
<td>70</td>
</tr>
<tr>
<td>No.</td>
<td>Solution</td>
<td>Solvent</td>
<td>Soaking temperature (°C)</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>-------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>8.</td>
<td>1 eq. of LB + 6 eq. of DMC + 3 eq. of HMDA + catalyst</td>
<td>Dioxane/water (8/2)</td>
<td>70</td>
</tr>
<tr>
<td>9.</td>
<td>LB</td>
<td>Dioxane/water (8/2)</td>
<td>70</td>
</tr>
<tr>
<td>10.</td>
<td>Patent by Bernard*</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Note: Solution was synthesized first by using 0.0906 mol of glycerol, 0.182 mol of DMC, \(4 \times 10^{-4}\) mol of phosphazene P_1-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 in order to solubilize them before being impregnated. However, when ethanol was the solvent of impregnation, pre-polymerization was held for about 30 minutes at the 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 solvent. In other cases, two-step impregnation was also performed by using pure polyol in the first impregnation, and alkyl carbonate and diamine in the second impregnation. Five different conditions of two-step impregnations performed were listed in Table 3.

### Table 3: Five different conditions of two-step impregnations

<table>
<thead>
<tr>
<th>No.</th>
<th>Solution</th>
<th>Impregnation I</th>
<th>Impregnation II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Reagents</td>
<td>Solvent</td>
</tr>
<tr>
<td>1</td>
<td>Cyclic carbonate of xylitol</td>
<td>Without solvent</td>
<td>HMDA</td>
</tr>
<tr>
<td>2</td>
<td>Cyclic carbonate of xylitol</td>
<td>Water</td>
<td>HMDA</td>
</tr>
<tr>
<td>3</td>
<td>Cyclic carbonate of xylitol</td>
<td>Ethanol</td>
<td>HMDA</td>
</tr>
<tr>
<td>4</td>
<td>Sorbitol</td>
<td>Water</td>
<td>DMC/HMDA (2/1)</td>
</tr>
<tr>
<td>5</td>
<td>LB</td>
<td>Dioxane/water (8/2)</td>
<td>DMC/HMDA (2/1)</td>
</tr>
</tbody>
</table>

Wood impregnation was carried out under full cell method. Oven dried beech (Fagus sylvatica) blocks were placed into a beaker in a desiccator, and vacuum of 0-1 mbar was drawn for about 15 minutes using a pump. The pressure was then released allowing the reagent solution to cover and impregnate the wood blocks. After 2 hours soaking (under 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 of

\[ WPG \% = \frac{m_1 - m_0}{m_0} \times 100 \]
where $m_0$ is the oven-dried weight of untreated wood samples and $m_1$ is the oven-dried weight of impregnated wood samples.

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.

**Chemical Leachability**

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 (1h, 2h and 4h) by replacing the water in between. The volume of the water used was fivefold of the total samples volume. The oven-dried weight of leached wood samples ($m_2$) was then used to calculate leached chemical (LC) expressed as percentage of the initial impregnated chemicals calculated by the following formula.

$$LC\% = \frac{m_2 - m_1}{m_1 - m_0} \times 100$$

**3 RESULTS**

**Liquefaction of Spruce Bark**

The liquefied spruce bark (LB) contained glycerol and a large number of hydroxyl groups from lignin or polysaccharides. The yields of liquefaction are listed in Table 4.

<table>
<thead>
<tr>
<th>Bark content (g)</th>
<th>S/L ratio</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1/4</td>
<td>72.6</td>
</tr>
<tr>
<td>50</td>
<td>1/4</td>
<td>47.9</td>
</tr>
<tr>
<td>10</td>
<td>1/7</td>
<td>77.0</td>
</tr>
</tbody>
</table>

Table 4 shows that in the same solid to liquid ratio, the higher the bark content, the lower the yield obtained. Increasing the solid to liquid ratio has brought about the slightly higher yield. The amount of solvent used seemed to only slightly influencing the liquefaction yield. Therefore, the ratio of 1/4 was further used for the liquefaction process in order to compromise between liquefaction performance and the cost of solvent.

**Solubility of Reagents**

Xylitol, sorbitol, glycerol and PG3 were well soluble in distilled water, but were not directly in alcohol, except for that of xylitol. Xylitol was partly soluble in methanol or ethanol at 50°C. The LB was soluble in distilled water, alcohols (methanol or ethanol) and in co-solvent of dioxane: water (80 : 20) after sonification.
The DMC was well soluble in distilled water at the 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 types of solvent. 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. This 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 used 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.

**Synthesis of Polyurethane**

**Non-solvent Two pot method**

In a non-solvent two pot reaction, initially xylitol was insoluble in DMC. At the end of this reaction, one-phase liquid obtained was then analyzed by FTIR. The spectrogram of the FTIR is shown in Figure 2.

![FTIR spectrum of the reaction products between xylitol and DMC](image)

The important functional groups characteristic in Figure 2 was the existence of cyclic carbonate with a vibration band of 1778 cm$^{-1}$. The band of 3003 cm$^{-1}$ was belong 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 by Figure 3. Both spectra show a band at about 1704 cm$^{-1}$ as a characteristic of the C=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 indicates the presence of urethane function.

At the end of this polymerization reaction, the product found was completely liquid with no solid residue. This result leads to the possibility of a non-solvent polyurethane (carbamate) synthesis.

**Two pot method in distilled water and alcohol**

Figure 4 indicates the FTIR spectrogram of two pot reaction 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 transcarbonatation product when the reaction were carried out in water. Instead, the presence of 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 the fundamental vibration of a molecule which is affected by the complexity or the overlapping/multiple of the frequency absorbed (Pineda-Harrera 2007). The weak band at 2940 cm\(^{-1}\) corresponds to the elongation vibration of the \(-\text{CH}\) bond.
Figure 4. The FTIR spectra of the cyclic carbonate of xylitol and sorbitol prepared in water and methanol.

After addition of DETA to these reactions, there is no carbamate function found in the reactions in water. This result confirmed the degradation of cyclic carbonate in aqueous medium. Nevertheless, a carbamate functional group at 1700 cm$^{-1}$ was appeared when reaction was carried out in methanol (Figure 5).

Figure 5. The FTIR spectra of the polyurethane found from reactions of xylitol and sorbitol prepared in methanol.
The FTIR spectra of the carbonate cyclic formation by using DEC and DMC (Figure 4) show similar characteristics. However, the use of DMC was simpler than that of DEC since the later 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 with those of sorbitol as polyol in the same condition (Figure 4 and 5).

One pot method

One pot reactions of polyurethane formation using different diamines gave FTIR spectra as shown in Figure 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.

The visual appearance of polymers varies considerably by the diamine used. The use of HMDA resulted in a solid product that less water-soluble compared to that resulted from the use of EDA and DETA. Therefore, HMDA was used for further polyurethane synthesis.

The best ratios of DMC/HMDA for each polyol according to the physical appearance of polymer produced are listed in Table 5. These ratios then used to prepare the solution for wood impregnation.

Table 5. Best ratio of DMC / HMDA for each polyol

<table>
<thead>
<tr>
<th>Polyol (one equivalent)</th>
<th>Number of equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMC</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>10</td>
</tr>
<tr>
<td>Xylitol</td>
<td>8</td>
</tr>
<tr>
<td>PG3</td>
<td>6</td>
</tr>
<tr>
<td>LB</td>
<td>6</td>
</tr>
</tbody>
</table>
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 6. 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 6. Molecular weight ($M_w$) of polyurethanes determined by SEC analysis.

<table>
<thead>
<tr>
<th>Polyl (1 eq.)</th>
<th>Eq. of DMC</th>
<th>Diamine</th>
<th>Solvent</th>
<th>Method</th>
<th>$M_w$ (g/mol)</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG3</td>
<td>6</td>
<td>3 HMDA</td>
<td>Water</td>
<td>OP</td>
<td>651</td>
<td>1.06</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>10</td>
<td>5 HMDA</td>
<td>Water</td>
<td>OP</td>
<td>748</td>
<td>1.02</td>
</tr>
<tr>
<td>Xylitol</td>
<td>8</td>
<td>4 EDA</td>
<td>Water</td>
<td>OP</td>
<td>603</td>
<td>1.01</td>
</tr>
<tr>
<td>Xylitol</td>
<td>8</td>
<td>4 EDA</td>
<td>Methanol</td>
<td>OP</td>
<td>1923</td>
<td>1.05</td>
</tr>
<tr>
<td>Xylitol</td>
<td>8</td>
<td>4 HMDA</td>
<td>Methanol</td>
<td>OP</td>
<td>3404</td>
<td>1.19</td>
</tr>
<tr>
<td>Xylitol</td>
<td>8</td>
<td>EDA/HMDA</td>
<td>Water/methanol</td>
<td>OP</td>
<td>674</td>
<td>1.01</td>
</tr>
<tr>
<td>Xylitol</td>
<td>4</td>
<td>2 HMDA</td>
<td>Without solvent</td>
<td>OP</td>
<td>4380</td>
<td>1.28</td>
</tr>
<tr>
<td>LB</td>
<td>6</td>
<td>3 HMDA</td>
<td>Water</td>
<td>OP</td>
<td>350</td>
<td>1.18</td>
</tr>
<tr>
<td>Xylitol</td>
<td>8</td>
<td>4 HMDA</td>
<td>Ethanol</td>
<td>TP</td>
<td>2344</td>
<td>1.05</td>
</tr>
<tr>
<td>Patent by Bernard (2008)*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1408</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Note: OP = one pot; TP = two pot

* = a reaction using 0.0906 mol of glycerol, 0.182 mol of DMC, 4 x $10^{-4}$ mol of phosphazene $P_{1-t}$-Bu catalyst, and 0.045 mol of HMDA at 100°C under magnetic agitation for one night in a flask equipped with a condenser

Table 6 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 higher molecular weight than that of using EDA.

Wood Impregnation

One-step impregnation

An impregnation by using sorbitol, DMC and HMDA in water under room temperature was carried out and gave WPG about 15.18%. The LC obtained under these conditions was 62.80% (Figure 7) and this was thought 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 its stoichiometry of this substance were then identified by FTIR spectroscopy, SEC and NMR. The FTIR spectrum is shown in Figure 8. The SEC analysis indicated that the average molar mass ($M_w$) of the substance was 283 g/mol. The $^1$H- and $^{13}$C-NMR spectra of this substance were shown in Figure 9 and 10.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Conditions</th>
<th>WPG (%)</th>
<th>LC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbitol</td>
<td>at 70°C</td>
<td>14.85</td>
<td>57.57</td>
</tr>
<tr>
<td></td>
<td>at room temperature</td>
<td>15.18</td>
<td>62.80</td>
</tr>
<tr>
<td></td>
<td>at 0°C</td>
<td>15.44</td>
<td>55.75</td>
</tr>
<tr>
<td>Xylitol</td>
<td>in ethanol (prepolym. 30 min. at 50°C)</td>
<td>12.59</td>
<td>50.36</td>
</tr>
<tr>
<td></td>
<td>in distilled water</td>
<td>14.29</td>
<td>51.14</td>
</tr>
<tr>
<td></td>
<td>without solvent (prepolym. for 1h at 70°C)</td>
<td>19.11</td>
<td>78.39</td>
</tr>
<tr>
<td>LB + 6 DMC + 3 HMDA + cat. (at 70°C)</td>
<td>without solvent (prepolym. for 1h at 70°C)</td>
<td>21.25</td>
<td>87.63</td>
</tr>
<tr>
<td></td>
<td>in dioxane/water (8/2)</td>
<td>19.71</td>
<td>56.43</td>
</tr>
</tbody>
</table>

At the end of this impregnation a white solid substance was formed. The chemical structure and its stoichiometry of this substance were then identified by FTIR spectroscopy, SEC and NMR. The FTIR spectrum is shown in Figure 8. The SEC analysis indicated that the average molar mass ($M_w$) of the substance was 283 g/mol. The $^1$H- and $^{13}$C-NMR spectra of this substance were shown in Figure 9 and 10.
Figure 8. FTIR spectrum of the diurethane produced by the reaction between DMC and HMDA
Figure 9. 1H-NMR spectrum of the diurethane produced by the reaction between DMC and HDMA.
The presence of carbamate functions is clearly indicated by the bands of 1700 and 1540 cm$^{-1}$ in Figure 8. The $^1$H-NMR spectrum confirmed a well-defined structure, corresponding to a dimethyl-1,6-hexanediylbis carbamate or simply named diurethane, formed by the secondary reaction between DMC and HMDA (Figure 9). The peak at 3.787 ppm corresponds to two methyl groups (-CH$_3$) of DMC. The peaks at 2.68 ppm, 1.49 ppm and 1.36 ppm were assigned to the three
types of methylene groups present in the molecule (SDBS 2012). The $^{13}$C-NMR spectrum of the substance confirmed the structure of diurethane as assumed by $^1$H-NMR (Figure 10).

The secondary reaction between DMC and HMDA in the aqueous solvent was undesirable since the DMC was expected to initially react with polyol before reacting with HMDA. With an average molar mass of 283 g/mol, the diurethane hindered the penetration of the reagents into 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 condition.

In order to avoid the secondary reaction of diurethane formation, several impregnations were performed in different soaking temperature of 0°C and 70°C. These impregnations gave WPGs of 15.18% and 15.44%, respectively, and LCs above 55%. The poor result was confirmed by the low degree of polymerization of polyurethane synthesized in water as shown in Table 4. These confirmed the occurrence of diurethane producing secondary reaction between DMC and HMDA. It also indicated that diurethane with low molecular weight was formed preferentially during the reaction in aqueous medium rather than in an alcoholic medium.

Non-solvent, in water and in ethanol impregnation of xylitol, DMC and HMDA were performed. Non-solvent impregnation increased WPG of 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.

Several impregnations using the liquefied spruce bark (LB) were performed under different conditions (see Table 2). Impregnation of LB in dioxane/water (8/2) with DMC and HMDA resulted in WPG of 19.71 %. The similar WPG was resulted from the impregnation of LB pure in the same solvent. The LCs obtained from these impregnations were almost similar; 50.36% for LB pure and 55.13% for LB with DMC and HMDA, both in dioxane/water (8/2).

The LC of non-solvent impregnation of LB and xylitol was about 21.25% and 19.11%, respectively. This could be explained by the results of SEC analysis of its prepolymers. The $M_w$ of prepolymer formed by xylitol, DMC and HMDA was 1326 g/mol after prepolymerization for 1 h at 70°C. The $M_w$ of prepolymer formed by LB, DMC and HMDA was 1204 g/mol after prepolymerization for 1 h at the same temperature.

As comparison, a non-solvent impregnation (100% concentration) was also performed based on the patented finding of Bernard (2008) that resulting in a WPG of 91.38%. The resulting LC of 51.41% was even less encouraging. These results is currently unexplainable from the perspective of the water solubility of poly(hydroxy)urethane.

**Two-step impregnation**

Several two-step impregnations were performed and the resulting data of their WPGs and LCs are shown in Figure 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 WPG$_1$ (6.82 %) was found quadruplicate of WPG$_2$ (23.91 %) in two-step impregnation.
with the absence of solvent (Figure 11, No. 1). 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 the total weight gained of 28.92% and 23.27%, respectively and the LCs of 43.08 % and 42.22 %, respectively. This is a noteworthy finding due to the fact that the one-step impregnation in water resulted in a lower WPG (approximately 15%) and LC of about 55% (see Table 6). Separated transcarbonatation reaction (cyclic carbonate synthesis) and diamine addition possibly prevented the formation of diurethane through secondary reaction.

![Figure 11. Weight Percent Gain (WPG) and percentage of leached chemicals (LC) of the two-step impregnations](image)

Separated impregnations of sorbitol and DMC/HMDA gave 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 %, Figure 7).

Two-step impregnation of LB and DMC/HMDA was also performed. The weight gain of LB impregnation was almost tenfold greater than that of DMC/HMDA impregnation. LB was also found soluble in water, thus tended to bring about a high LC of 56.52% when impregnated.
4 DISCUSSION

Liquefied Spruce Bark

The optimum yield obtained from this study was about 72.6% with a bark to glycerol ratio of 1 to 4. Higher liquefaction yield was reported by Mun et al. (2002). A liquefaction of Pinus radiata bark using phenol as solvent (liquor ratio of 2) and sulfuric acid as catalyst at temperature 150°C for 120 minutes gave a yield of 90.8%. However, a yield of 97.8% was obtained from a different catalyst p-toluenesulfonic acid in the same liquefaction condition. Phenol was known effective to liquefy the high lignin content biomass like bark. However, it contributes environmental pollution and high recovery cost. The phenol removal from liquefaction product is also difficult (Hassan and Mun 2002).

Hassan and Shukry (2008) has investigated the effect of liquefaction temperature and reported that the higher temperature of liquefaction (until a certain optimal point) allows the higher yield. In their study on the liquefaction of cotton stalk and bagasse in acidic binary solvent of PEG#400/glycerin (9/1), the increasing of liquefaction temperature to 150°C gave lower liquefaction residue. The optimum temperature reported was then 150°C for the increasing to above 150°C only diminished slightly the residue. Brosse et al. (2010) has also reported that heat treatment leads to polysaccharides degradation (especially hemicelluloses) and lignin depolymerization and deconstruction by breaking α and β-aryl-ether linkages.

Liquefied bark was known as rich of phenolic resin content, valuable and potential for other uses i.e. adhesives, foams (Zhao et al. 20012; Ge et al. 2000), wood coating, particleboard. The use of liquefied bark as polyol for polyurethane preparation was also investigated by Ge et al. (2000). He has reported that the higher density and resilience value of polyurethane foams (PUFs) produced was given by the higher content of liquefied bark of Acacia mearnsii as it contain of high wattle tannin to crosslink and improve the PUFs properties. The bark was liquefied in an acid catalyst method using poly(propyleneglycol) (PPG), glycerol, and sulfuric acid catalyst with a weight ratio of 94/5/1.

Synthesis of Polyurethane

The formation of cyclic carbonate of xylitol in distilled water faced inconvenient i.e. degradation of the cyclic carbonate. The differ of temperature gave no different result. It is therefore necessary to carry out the synthesis of polyurethane in a non-aqueous solvent, a solvent that can prevent 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 appear to be the best candidates to meet these conditions.

Duchanois (2011) reported that the cyclic carbonate is more reactive with primary amines in water. Therefore, the synthesis of polyurethane 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 Figure 6, the less-soluble characteristic of the product from the use of HMDA was thought due to the HMDA hydrophobic character (Duchanois 2011). This was why the HMDA was then chosen to the subsequent works in a non-isocyanate synthesis of polyurethanes.

To simulate the one-pot method that respect to 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 directly the desired polymer. This method allows the formation of polymer from the first hour of reaction. However, the resulting polymer was still soluble in water, and thus failed to result in a less leachable polymer that can be applied in wood. The evaporation of DMC during the reaction might be indicative to 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.

**Average Mass Distribution**

Diamine structure was reported to influence the molecular weight of the polymer resulted, in which the higher the molecular weight of diamine, the higher the molecular weight of the resulting polymer (Steblyanko et al. 2000). 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 to 4380 g/mol. The synthesis of polyurethane using one-pot method has been recommended by the patent of Bernard (2008). Unfortunately, it is not applicable industrially to impregnate wood without solvent. It is also difficult to maintain the stoichiometry of the reaction during impregnation and in-site polymerization (Duchanois 2011).

The synthesis of polyurethane through 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 two-pot method gave lower $M_w$ of 2344 g/mol (Table 3).

Later research of Rokicki and Piotrowska (2002) was investigating the polycondensation of $[n,m]$polyurethane, through a reaction between a hydroxy-urethane with longer-chain diols. The polymer produced from 1,6-bis(hydroxyethyloxy carbonylamino)butane and 1,10-decanediol using a xylene as azeotropic solvent for glycol removing from reaction system (reaction under 145-150°C) was in $M_w$ of 3040 g/mol. Another reaction using 1,6-bis(hydroxyethyl oxy carbonylamino)hexane in the same condition gave a higher $M_w$ polymer of 6300 g/mol. It is interesting to know that the addition of longer-chain diols to the poly(hydroxy-urethane) would potentially produce a higher degree of polymerization of 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. This is confirmed by the product obtained from a reaction with cyclic carbonate of xylitol and HMDA using phosphazene P$_{t-Bu}$ as catalyst. The product obtained has a molecular weight of 1408 g/mol. Indeed, synthesis of polyurethane in two-pot method reduces the degree of polymerization (DP), and lead to larger leaching or smaller oligomers (Table 8 and Figure 11) (Duchanois 2011).
Wood Impregnation

Figure 7 and 11 show that the highest WPGs and lowest LCs were belongs 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 against leaching than the branched polymer (Vriet 2005).

Figure 7 shows also poor results from the one-step impregnations using water as solvent. The low WPGs (about 15%) and the high LCs (above 55%) represent an unacceptable result for an industrial application. This poor result may be caused by an inevitable formation of diurethane by the secondary reaction, even with changing the temperature. The only interaction between the diurethane and wood is Van der Waals bonds, made by the functions -NH (carbamate). The diurethane was therefore easily removed by water during leaching (Durchanois 2011). The poor result was confirmed by the low degree of polymerization of polyurethane formed as shown in Table 6.

5 CONCLUSION

Synthesis of polyurethane by using no solvent gives a polymer with a high degree of polymerization (DP). 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 with the impregnation with an aqueous solution. However, the results of impregnation by polymers obtained from an alcoholic solution face a problem when used outdoor due to their leaching.

Synthesis of polyurethane in an aqueous medium allows degradation of cyclic carbonate and thus reduces the urethane function produced. However, synthesis in alcoholic medium gives larger polyurethane.

In view of these results, the testing of these polymers against termites and fungi on wood specimens treated and leached are very important. 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 on 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 industrial level, in the order of a method environmentally friendly entering a general context of sustainable development and low toxicity to humans.
REFERENCES


Duchanois T. 2011. Utilisation de carbonates cycliques pour la synthèse de polyuréthanes dans le cadre de la mise au point d’une méthode verte de modification chimique du bois. Thesis. Chimie Verte. Université de Strasbourg, France


Hassan EM, Mun SP. 2002. Liquefaction of pine bark using phenol and lower alcohols with methanesulfonic acid catalyst. J Ind Eng Chem. 8 (No.4), 359-364


Hill CAS. 2006. Wood Modification : Chemical, Thermal and Other Processes. School of Agricultural and Forest Sciences, University of Wales, Bangor : John Wiley & Sons, Ltd


AUTHOR BIOGRAPHY

The author was born in Kabanjahe, Karo, North Sumatra, on June 30th, 1987 from father Saur P. Sitanggang and mother Dra. Rugun Naibaho. The author is the youngest daughter of four siblings.

In 2005, the author graduated from SMAN 1 Kabanjahe and continued her study on Bachelor degree in Forest Products Technology Program, Faculty of Forestry, Bogor Agricultural University (IPB) through Undangan Seleksi Masuk IPB (USMI).

The author was a lecture assistant on Christian Religion in year 2006/2009, and on Pulp and Paper in 2008-2009. The author gained her Bachelor degree’s of Forestry from IPB in 2010 and continued her study to Master Program with scholarship called “Beasiswa Unggulan” from the Ministry of Education of Indonesia. The scholarship was held as double degree program with the implementation of the first year in Indonesia (IPB) and the second year, including research in University of Lorraine, Nancy, France.